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Geochimica et Cosmochimica Acta

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The Novo Urei meteorite

A. E. Ringwood
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(*Received* 3 *March* 1960)

Abstract—The occurrence of diamond in Novo Urei has been confirmed by X-ray diffraction. Chemical and mineralogical studies of this meteorite suggest that it is an intensely metamorphosed chondrite.

Introduction

A chemical and mineralogical study of the Novo Urei ureilite was carried out by Jerofejeff and Latschinoff (1888). After intensive chemical decomposition of a sample, they found 2·26 per cent of inert carbonaceous residue, of which 1 per cent was identified as diamond and the remainder as graphite. Identification was based upon such properties as density, hardness, inertness to chemical reagents and combustion. Subsequently Kunz (1888) verified that the meteorite contained a substance which was capable of scratching sapphire.

Urey (1956) pointed out that the occurrence of diamond in stone meteorites is of considerable genetic importance as an indicator of the pressure under which meteorites formed, and therefore, of the minimum sizes of the parent bodies from which they are derived. It therefore seemed most desirable to confirm Jerofejeff and Latschinoff's identification by X-ray diffraction.

Experimental

A piece of Novo Urei weighing approximately 1·5 g was presented by the Australian Museum, Sydney. This was crushed to −150 mesh in a steel mortar, and 0·9882 g were taken for chemical investigation. The sample was digested in a platinum dish with a mixture of dilute (1:1) hydrochloric and nitric acids. After reaction had ceased it was dried on a steam bath. Hydrofluoric acid (25 ml) and concentrated sulphuric acid (8ml) were added and the solution evaporated to dryness. The product was then dissolved in dilute sulphuric acid and separated from the unreacted residue which was washed and dried. The separated sulphate solution containing all the cations originally present in the meteorite was evaporated to dryness in a platinum dish and set aside for chemical analysis.

The undissolved residue was a fine grained black powder weighing 0·0236 mg. Under the microscope, a few very minute crystals were observed to have a refractive index higher than 2·0, but most of the material was indeterminate. An X-ray powder pattern using Cu radiation was taken (Fig. 1) and showed the black material to consist of approximately equal quantities of diamond and graphite, together with some platinum derived from the dish. Jerofejeff and Latschinoff's conclusion was thus fully confirmed both qualitatively and quantitatively.

A second sample of the meteorite (−150 mesh) was subjected to magnetic separation with a hand magnet. It proved rather difficult to separate the metal

cleanly, since much of it apparently occurred as small inclusions in the silicates. The most magnetic fraction was X-rayed, using a powder camera and cobalt radiation. It was found to consist of kamacite with a lattice parameter of 2·8672 Å. This indicates the presence of only 2 per cent of nickel in solid solution (Owen and Burns, 1939), the lowest amount found in the metal phase of any meteorite known to the writer. The powder pattern showed that no taenite was present.

An optical investigation was carried out on the silicate fraction. Olivine and pyroxene were the only minerals identified. The refractive indices of olivine were $\alpha = 1{\cdot}676$ and $\gamma = 1{\cdot}712$, indicating 21 mole per cent of Fe_2SiO_4. Clinopyroxene had $\alpha = 1{\cdot}676$, $\gamma = 1{\cdot}691$ and an extinction angle of 38°. Assuming the pyroxene to be a pure Mg–Fe variety this would indicate about 18 mole per cent of $FeSiO_3$. This is likely to be somewhat high, since a small amount of Ca and Al are probably in solid solution.

Table 1. Chemical analyses of Novo Urei

	1	2	3	4
SiO_2	39·51	40·76	38·04	
MgO	35·80	36·91	23·84	56·4
FeO	13·35	16·58	12·45	34·1 (Fe_2O_3)
CaO	1·40	1·05	1·95	1·60
Al_2O_3	0·60	0·39	2·50	0·60
Cr_2O_3	0·95	0·45	0·36	0·69
Na_2O		0·45	0·98	0·69
MnO	0·43	0·36	0·25	0·55
P_2O_5	0·02	0·07	0·21	0·11
TiO_2		0·09	0·11	0·13
Ni	0·20	0·16	1·34	0·31 (NiO)
Fe	4·99	2·73	11·76	
C	2·26			
FeS	0·41		5·73	

Column 1. Jerofejeff and Latschinoff.
Column 2. This work, recalculated from column 4 as described in text.
Column 3. Average chondrite Urey and Craig (1953).
Column 4. Soluble bases from decomposed sample.

It seemed desirable to check the chemical analysis by Jerofejeff and Latschinoff (Table 1, column 1). Accordingly the evaporated filtrate containing the cations present in the meteorite was analysed by Mr. R. L. Lewis of the Australian Mineral Development Laboratories (column 4). This could not be directly compared with Jerofejeff and Latschinoff's analysis, since the silicon had been lost during decomposition as SiF_4. In addition, total iron only could be determined.

To enable a comparison to be made, it was assumed that the SiO_2/MgO ratio found by Jerofejeff and Latschinoff would apply to the present specimen. Total iron was partitioned between FeO and Fe metal by using the optically determined FeO/(FeO + MgO) ratio of the silicates. All the nickel was included with the metal phase. The resultant analysis is set out in column (2).

Agreement between Jerofejeff and Latschinoff's analysis and the present one is quite good. The chief difference is the presence of 0·45 per cent Na_2O in the

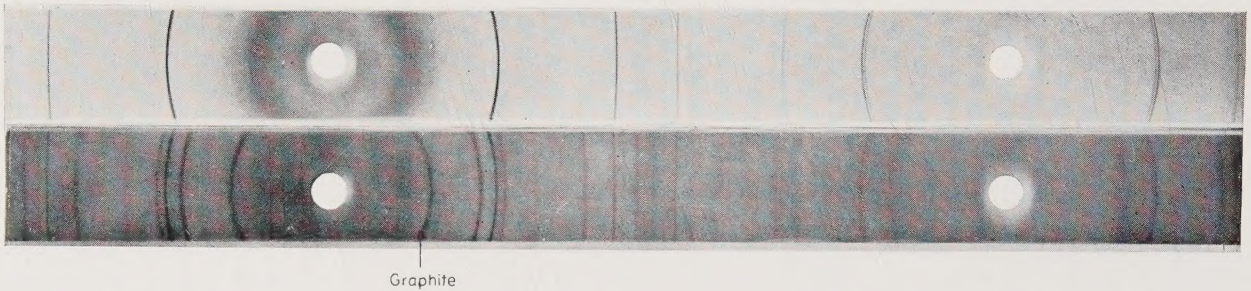
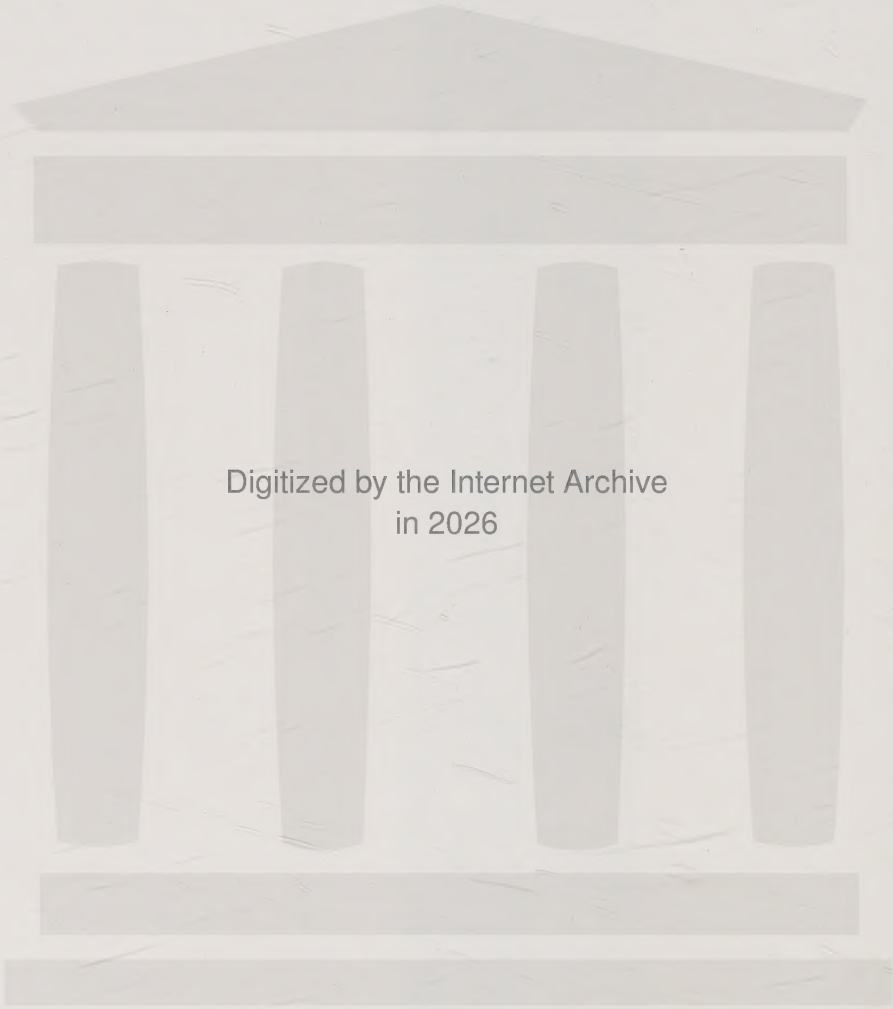


Fig. 1. Above. Natural diamond. (Weak low angle lines are caused by impurities). Below. Diamond and graphite in residues from Novo Urei. The extra lines belong to platinum impurity derived from the crucible.



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new analysis. JEROFEJEFF and LATSCHINOFF did not determine this constituent. The higher value obtained by JEROFEJEFF and LATSCHINOFF for the metallic iron content is probably more correct since they made a direct determination.

DISCUSSION

A large amount of information on the conditions necessary for diamond stability is available (e.g. BOVENKERK *et al.*, 1959). It seems improbable that diamonds can form metastably, or that they are likely to form below 1000°K even over long periods of time. Thus the presence of diamond infers that Novo Urei has been formed under a pressure approximating 35,000 atm.

Additional evidence indicative of high pressure is available. Although an appreciable amount of sodium and aluminium are present, no plagioclase was identified by the writer in the small specimen examined. This suggests that these components occur as jadeite in solid solution in the pyroxene. Such behaviour would be anticipated under high pressure.

Microscopic study shows that a large number of olivines and pyroxenes are poorly crystallized, being full of small opaque inclusions of metal, carbon and sulphide. The appearance suggests that Novo Urei is of metamorphic origin. It is unlikely that these textures would have been retained if crystallization had been from a completely molten state.

The mineralogy of Novo Urei and other ureilites resembles that of chondrites. The principal minerals present in both cases are olivine, pyroxene and nickel-iron. The chemical compositions are generally similar, although some differences exist, which will be discussed subsequently. If one examines a large number of chondrites, a complete transition is observed between porous, tuffaceous types, rich in chondrules, through to crystalline, coherent types with low porosity. Optical examination shows that the transition is due to metamorphism (MERRILL, 1921) which causes compaction, recrystallization, and slight mobilization of components. The metamorphic recrystallization may be sufficient to obscure the formerly chondritic textures.

In view of the relationships discussed above it would seem plausible to regard Novo Urei essentially as an intensely metamorphosed chondrite in which extensive recrystallization and grain growth have obscured the original chondritic texture. An analogous origin would be suggested for other ureilites such as Goalpara, in which UREY *et al.* (1958) have previously found diamond.

There are some differences between the analysis of Novo Urei and that of an average chondrite (Table 1). Nickel, sulphur, iron, sodium and aluminium are relatively deficient in Novo Urei. It may be significant that these elements would be concentrated in the liquid phase if a typical chondrite had been subjected to a small degree of partial melting. Fe, Ni, FeS and NiS are miscible in the liquid phase and have respective melting points of 1535°C, 1455°C, 1193°C and 797°C. Thus one would expect the earliest liquid formed by fractional melting in this system to be rich in sulphur and nickel. Similarly, from known phase relationships we might expect sodium and aluminium to be concentrated in the first-formed silicate liquid fraction. Thus the compositional abnormalities of Novo Urei might be explained if it had been subjected to metamorphism sufficiently intense to

cause the formation of a small amount of liquid* which subsequently migrated or was squeezed elsewhere.

The relationships previously inferred between ureilites and chondrites imply that these meteorites were derived from a parental planetary body at least as large as the moon. The increasing degrees of coherence and metamorphism observed in passing through the many varieties of chondrites to the ureilites would be correlated on this basis, with increasing depth of origin within the parent body.

Acknowledgements—The writer acknowledges the generosity of Mr. O. CHALMERS and the Australian Museum, Sydney, who donated their only specimen of Novo Urei for the present investigation.

REFERENCES

BOVENKERK H. P., BUNDY F. P., HALL H. T., and WENTORF R. H. (1959) *Nature, Lond.* **184,** 1094.

JEROFEJEFF M. and LATSCHINOFF P (1888) *Verh. Russ. Iais. Min. Gesell. St. Petersburg* 2nd Ser. **24,** 263.

KUNZ G. F. (1888) *Science* **11,** 118.

MERRILL G. P. (1921) *Bull. Geol. Soc. Amer.* **32,** 395.

OWEN E. A. and BURNS B. D. (1939) *Phil. Mag.* **28,** 497

UREY H. C. (1956) *Astrophys. J.* **124,** 623.

UREY H. C. and CRAIG H. (1953) The composition of the stone meteorites and the origin of the meteorites. *Geochim. et Cosmochim. Acta.* **4,** 36–82.

UREY H. C., MELE A. and MAYEDA T. (1958) Diamonds in stone meteorites. *Geochim. et Cosmochim. Acta* **13,** 1–4.

* It may be most significant, that BOVENKERK *et al.* (1959) found that the experimental formation of diamond from graphite or other forms of carbon required the presence of a liquid-metallic catalyst. Molten nickel was found to be the most satisfactory catalyst, whilst both molten iron and a solution of iron sulphide in iron were found to be satisfactory.

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Cosmogenic nuclear reactions in iron meteorites*

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(*Received* 10 *February* 1960)

Abstract—The cosmogenic He^3, He^4, Ne^{21}, Ne^{22}, Ar^{36} and Ar^{38} isotopes have been measured mass spectrometrically in seven ataxites and one octahedrite. An attempt at analysis of these and previous data is made based on nuclear reactions induced by high-energy protons. A combination of He^3/He^4, He^3/Ar^{38} and Ne^{21}/Ar^{38} ratios are used as a measure of the energy and intensity of the incident radiation. Factors contributing to anomalous ratios are discussed. Exposure ages are deduced on the basis of these ratios, total isotopic abundances, and previously measured Cl^{36} values.

Introduction

Early experimenters (Arrol *et al.*, 1942) on the rare-gas contents of meteorites attributed the helium found to the radioactive disintegration of uranium and thorium. By quantitatively measuring these elements they attempted to determine ages for these meteorites. However, a number of these ages were greater than any reasonable estimate of the age of the solar system. Bauer (1947, 1948a,b) and Huntley (1948) then independently proposed that the meteorites may be subject to cosmic radiation such that nuclear reactions will be induced, and helium would clearly be a result of these reactions. Bauer went on to point out that helium-3 would be formed in an amount greater than its terrestrial isotopic composition, and to suggest the existence of a depth effect. The presence of this excess helium-3 has been experimentally confirmed. Several investigators (Paneth *et al.*, 1953) have reported the existence of the depth effect, while others (Gerling and Levskii, 1958) did not find it. The helium-3/helium-4 ratio has been found in most iron meteorites to lie between 0·2 and 0·35. This ratio indicates that nuclear reactions occur frequently in meteorites, and other product nuclides have been looked for. Cosmogenic neon and argon isotopes have been found (Reasbeck and Mayne, 1955; Gentner and Zähringer, 1957). The neon and argon are formed presumably as spallation products; the helium is formed from direct knock-on processes and as evaporated particles from an excited nucleus.

Since these nuclides have been formed by the action of cosmic radiation, it seems possible to study the composition and history of the radiation by measuring these and some radioactive products. It may also be possible to obtain information on the origin of meteorites, and thus on the history of, presumably, the solar system. Attempts have been made to ascertain cosmic-ray exposure ages by He^3/tritium ratios (Begemann *et al.*, 1957; Fireman and Schwarzer, 1957) and by He^3/Ar^{39} ratios (Fireman and Defelice, 1960). Such ages have also been calculated from measurements of single isotopes, in particular the helium-3 (Singer, 1958; Urey, 1959). There are, however, many difficulties in these calculations. A large portion of the helium may be produced in secondary reactions.

* Research performed under the auspices of the U.S. Atomic Energy Commission.

and it is dubious as to how well this can be accounted for in an object of indeterminate size and shape. The cross-sections on which these calculations are based are also not too well known. The additional uncertainties as to the energy and history of the cosmic radiation indicate that these ages are not too reliable a set of figures.

This paper is part of a series aimed at the measurement of isotopes of helium, neon and argon in various iron meteorites. It is hoped that the measurements of all these nuclides in the same metallic mass will help clarify the above situation. One should expect to obtain variations in the isotopic ratios and in addition variations in the He : Ne : Ar ratios, depending on the sample's depth in the meteorite and on the history of the meteorite.

Recently, measurements have been made (Schaeffer and Zähringer, 1960) on seven metorites, chosen for their varied helium content. The He^3/He^4 ratio was found to vary from 0·25 to 0·35, with one exception of 0·10. This last meteorite had a total helium content a factor of approximately 10 lower than the others. This seemed to be in line with the assumption that both He^3/He^4 ratios and total helium content will diminish towards the interior of an iron mass; the former due to considerations arising from nuclear reaction theory, the latter due to lower intensity of the incident radiation. These same nuclides have been measured (Schaeffer and Fisher, 1959) in another meteorite and a He^3/He^4 ratio of 0·067 was found, together with a higher helium content than any of the previously measured seven. It was postulated that the excess He^4 was radiogenic, and that the reason for its retention in this particular meteorite was the ataxite structure.

In this paper the rare gases have been determined in seven ataxite and one octahedrite iron meteorites. An attempt is made to interpret these and previous data in terms of nuclear reactions induced in iron by cosmic-ray protons, utilizing the results of high-energy cross-section measurements to set up criteria for estimating the production rates of various nuclides in each meteoritic sample, and thus estimating exposure ages.

Experimental

A high-sensitivity mass spectrometer and sample preparation system, capable of detecting accurately a few billion atoms, was used for the measurements. The apparatus is described in detail elsewhere (Schaeffer, 1959). Samples of each meteorite, weighing from 0·1 to 0·3 g, were placed in an alumina crucible within a molybdenum cup. This was surrounded by a quartz tube to separate it from the main line, which was constructed of Corning 1720 glass to inhibit helium diffusion. The sample was vaporized by heating with an induction heater at about 1800°C for 20 min. At the end of each series of runs there was no iron left in the crucible, each series consisting of about six meteorite samples. Blank runs were made between sample runs; the amount of helium-3 was negligible, helium-4 was a few per cent of an average sample, neon-20 and argon-40 were present in an amount equivalent to that found in the meteoritic samples. The amount of neon-21, neon-22, argon-36 and argon-38 due to background were calculated from terrestrial isotopic abundances and the measured neon-20 and argon-40 contents. Previously a graphite crucible had been used and the meteorites melted, but not

vaporized. This was changed because several early results lead to the possibility that the iron, upon first melting, formed a higher-melting carbide which trapped gases inside.

The meteorites studied here are described in the Appendix.

Table 1. Results of He-, Ne- and Ar-measurements in the present investigation in units of 10^{-8} sec

Meteorite	He^3	He^4	Ne^{21}	Ne^{22}	A^{36}	A^{38}
Forsyth Co.	46·5	158	0·59	$0·98 \begin{matrix}+0·1\\+0·5\end{matrix}$		
	50·0	145	0·59	$0·89 \begin{matrix}-0·1\\-0·3\end{matrix}$		
	52·0	157	0·58		1·4	2·2
	41·3	141	0·57	0·66 ± 0·1	1·3	1·9
Ave.	48 ± 6	150 ± 10	0·58 ± 0·05	0·84 ± 0·2	1·3 ± 0·2	2·1 ± 0·2
Santa Catherina	56·4	226	0·50	$0·62 \begin{matrix}+0·06\\-0·1\end{matrix}$	1·5	2·7
	57·1	226	0·45	0·52 ± 0·06	1·5	2·6
	55·4	227	0·51	0·61	1·9	3·1
	59·2	233	0·60			
Ave.	57 ± 6	228 ± 30	0·58 ± 0·1	0·58 ± 0·1	1·6 ± 0·2	2·8 ± 0·3
Santa Rosa	45·7	183	0·44	$0·62 \begin{matrix}+0·6\\-0·2\end{matrix}$	1·5	2·35
	44·8	187	0·43	$0·67 \begin{matrix}+0·1\\-0·2\end{matrix}$		
	51·3	183	0·44	$0·54 \begin{matrix}+0·06\\-0·1\end{matrix}$	1·4	2·25
Ave.	47 ± 5	184 ± 15	0·44 ± 0·04	$0·61 \begin{matrix}+0·06\\-0·1\end{matrix}$	1·5 ± 0·3	2·3 ± 0·4
Smithland	59·3	226	0·65			
	59·0	219	0·62	$1·12 \begin{matrix}+0·1\\-0·4\end{matrix}$	1·8	2·8
	55·3	187	0·58	0·61 ± 0·1	1·6	2·5
Ave.	58 ± 4	211 ± 25	0·62 ± 0·06	~0·9 ± 0·4	1·7 ± 0·3	2·6 ± 0·5
Tombigbee River	5·10	30·0				
	5·78	40·7	0·096 ± 0·04			
	4·04	32·4	0·071 ± 0·02	0·14 ± 0·1	0·26	0·38
	4·07	30·3	0·065 ± 0·02		0·30	0·36
Ave.	4·7 ± 1	33·4 ± 6	0·077 ± 0·02	0·14 ± 0·1	0·28 ± 0·3	0·37 ± 0·04
Tucson	12·3	153	0·78	0·85 ± 0·1	0·33	0·50
	13·4	141	0·80	0·80 ± 0·1	0·36	0·55
	13·0	151	0·85	0·77 ± 0·1		
Ave.	12·9 ± 1	148 ± 15	0·81 ± 0·08	0·81 ± 0·1	0·35 ± 0·04	0·53 ± 0·05
Washington Co.	193	2700	2·14	2·6	5·6	7·8
	193	3100	1·98	2·2	5·1	7·2
Ave.	193 ± 20	2900 ± 300	2·06 ± 0·2	2·4 ± 0·2	5·4 ± 0·5	7·5 ± 0·7
Canon Diablo	97·8	330	1·05	1·17	2·6	4·0
	90	310	0·88	0·93	2·8	4·6
Ave.	94 ± 9	320 ± 30	0·97 ± 0·1	1·05 ± 0·2	2·7 ± 0·3	4·3 ± 0·4

Results

The results of the mass spectrographic analysis of the meteorites are shown in Table 1. All the meteorites except Canon Diablo are ataxites. Cosmogenic neon-20 was not measured because of high backgrounds. For this reason it was also not always possible to determine the neon-22, and in those cases where it was determined the error is large, as indicated. The background for neon-21 was usually less than 10 per cent. Well over 90 per cent of the argon-40 is contamination; radiogenic argon-40 may also be present. In some cases the background correction for argon-36 was as high as 30 per cent. The argon-38 background was about 5 per cent.

Discussion

Radiogenic helium-4

In a previous paper (Schaeffer and Fisher, 1959) it was proposed that the low He^3/He^4 ratio found in the Washington County meteorite was due to the disintegration of uranium and thorium rather than to a cosmogenic process. It was thought that ataxites are not so liable to lose this radiogenic helium as are the octahedrites, as diffusion along crystal boundaries is mainly responsible for the loss (Urey, 1955). In the present paper, of six additional ataxites studied, two showed a low He^3/He^4 ratio. A value of 0·14 was found for Tombigbee River, but all the ratios and all the isotopic abundances were low for this meteorite, indicating it was at a great depth in the original body. Thus its He^3/He^4 ratio is not necessarily evidence of excess He^4. Tucson, however, has a He^3/He^4 ratio of 0·07 comparable to that of Washington County.

It thus seems possible that non-cosmogenic He^4 may be retained in the ataxite structure. The origin of this helium is presumed to be radioactive disintegration, although the possibilty of primordial helium cannot yet be ruled out. There are two consequences to our study: (1) The possibility exists of obtaining valid helium–uranium ages for some iron meteorites, and (2) it is possible that some of the He^4 in all meteorites is radiogenic, or that some of all the gases are primordial. This latter consideration may interfere with our calculations of exposure ages, but at least in those meteorites with "normal" He^3/He^4 ratios (in the range 0·20–0·35) it is not expected to be a serious consideration.

The cosmogenic rare gases

The central object of these studies is to account for the observed rare gas abundances in meteorites on the basis of measured nuclear reaction cross-sections, and in this manner to investigate the history of the meteorites. The accumulation of inert gases, assumed to be cosmogenic, will depend on (1) the length of exposure to the cosmic radiation, (2) the energy of the cosmic radiation, and (3) the intensity of the cosmic radiation. Factors (2) and (3) will in turn depend on the amount of shielding on each meteorite fragment, and this may be expected to vary from one to another. It is assumed that the results in meteorites can be interpreted by considering monoenergetic protons incident on an iron target. This neglects the smearing out of the cosmic radiation caused by the shielding of each meteorite, and the fact that there are several elements besides iron, notably nickel, present in the meteorites. We assumed that the rare gas ratios at 6 BeV most closely approximate the results of cosmic radiation, and that as the radiation is attenuated on passing through the meteorite it will lose energy so that the ratios may pass toward the experimental values found at lower energies.

Experiments have been in progress at this laboratory on the measurement of such rare-gas yields from high-energy proton bombardments of iron targets. Some results are summarized in Table 2.

Previous investigators (Hoffman and Nier, 1958, 1959; Fechtig *et al.*, 1960; Ebert and Wänke, 1957) have concerned themselves with the variation of the He^3/He^4 ratio at various depths in iron meteorites. The He^3/He^4 ratio was measured at different depths and an extrapolation was made based on the interaction

of high-energy protons and their secondary particles with iron. However, it is difficult to reconcile the He^3/He^4 ratio solely with proton-induced nuclear cross-section data because of several factors. It is estimated that about 20 per cent of the primary cosmic radiation consists of α-particles with a mean energy of 300 MeV per nucleon (NEHER, 1958). Some of these will undergo stripping reactions to produce He^3, many will come to rest in the meteorite without undergoing reaction, and some will initiate further nuclear reactions. These nuclear reactions of the α-particles can certainly be expected to produce a different He^3/He^4 ratio than will the nuclear reactions of protons. No experimental cross-section measurements

Table 2. Ratios of cross-sections from nuclear reaction measurements

Ratio	0·16 BeV*	0·43 BeV*	0·7 BeV†‡	6·0 BeV†§
$He^3 + T/He^4$	0·15	0·17	0·25	0·35
$He^3 + T/Ne^{21}$		770	85	38
$He^3 + T/Ar^{38}$		9·6	8·9	10
Ne^{21}/Ar^{38}		0·0125	0·10	0·265
Ar^{38}/Ar^{36}		8·0	8·1	8·0

* SCHAEFFER and ZÄHRINGER (1959).
† FISHER and SCHAEFFER, unpublished data.
‡ Tritium values from KUZNETSOV and MEKHEDOV (1959).
§ Tritium values from FIREMAN and ZÄHRINGER (1957).

for helium production have been carried out with such energetic α-particles. Another factor is the considerable variation in the published tritium cross-sections in proton-induced reactions. In meteorites the tritium decays with a 12 year half-life and is measured as He^3. Finally, it is not clear how accurately the cross-section measurements account for secondary nucleons and mesons. These secondaries will contribute significantly to the He^3 and He^4 production in meteorites.

In addition to these primarily nuclear considerations, trace elements in the meteorite can affect the ratios. The possibility exists of (n, α) and (p, α) reactions on Li^6. Each such reaction gives a He^3/He^4 ratio of unity. We have calculated that as few as 10^{16} Li^6 atoms/g would contribute significantly to the observed values. The Li^6 in a few meteorites has been studied (FIREMAN and SCHWARZER, 1957) and an estimate of less than 10^{16} atoms/g was made. Lower limits should be set on many more meteorites before this consideration may be disregarded. Other impurities can affect our values for neon and argon. (n, α) and (p, α) reactions on Mg^{24} contribute to the Ne^{21} in meteorites and these same reactions on K^{41} will increase the Ar^{38} content. There is also the possibility of radiogenic He^4 or primordial rare gases in iron meteorites, as discussed previously.

It would therefore seem useful to utilize all three ratios, He^3/He^4, Ne^{21}/Ar^{38}, and $He/^3Ar^{38}$, to determine the relative depths of the samples. In this manner, it is possible to pick out and reject a ratio that may be in error due to an impurity. Data obtained in this experiment together with previous data have been used to arrange fourteen iron meteorites in a proposed order of increasing depth in Table 3. Those rare gas contents which seem to be too high are listed as anomalous. The

Cl^{36} contents of several of the meteorites has been measured (Sprenkel, 1959) and these values are included in the table.

If the exposure age is long in comparison to the Cl^{36} half-life of $3{\cdot}1 \times 10^5$ years, the Cl^{36} activity gives a production rate. Comparing this with relative cross-sections as determined from high-energy bombardments and with isotopic contents of the rare gases in each meteorite, exposure ages can be estimated.

Table 3. Meteorites listed in proposed order of increasing depth

Meteorite	He^3 ($\times 10^{-8}$ scc/g)	Ne^{21}/Ar^{38}	He^3/Ne^{21}	He^3/Ar^{38}	He^3/He^4	Cl^{36} (d/m kg)	Anomalous
Toluca	100	0·33	125	42	0·34		
Casas Grandes	130	0·28	130	36	0·35	1·0	
Arispe	270	0·26	120	30	0·29		
Odessa	220	0·19	96	18	0·31	7·8	Ar^{38}
Sikhote Alin	130	0·37	86	32	0·27	6·9	Ne^{21}
Washington Co.	193	0·28	94	26	0·07		He^4
Tucson	13	1·5	16	25	0·09		Ne^{21}, H^4
Forsyth Co.	48	0·28	83	23	0·32		Ne^{21}
Canon Diablo	95	0·23	95	23	0·30	6·8	
Smithland	58	0·25	94	22	0·28		
Williamstown	480	0·23	80	18	0·25	3·3	
Santa Rosa	47	0·19	107	21	0·26		He^3
Santa Catherina	57	0·19	121	22	0·25		He^3
Carbo	350	0·19	100	19	0·24	3·6	He^3
Tombigbee River	4·7	0·12	61	7·4	0·14		

Table 4. Production rates of He^3, Ne^{21} and Ar^{38}

Meteorite	Cl^{36} (d/m kg)	Ar^{38}/Cl^{36}	Ar^{38} (scc/my g)	He^3/Ar^{38}	He^3 (scc/my g)	Ne^{21}/Ar^{38}	Ne^{21} (scc/my g)
Toluca Casas Grandes	8 ± 3	2	0·031	39	1·2	0·31	0·0096
Arispe Odessa Sikhote Alin Washington Co. Tucson Forsyth Co. Canon Diablo Smithland	7 ± 2	2	0·027	26	0·70	0·25	0·0068
Williamstown Santa Rosa Santa Catherina Carbo	4 ± 2	2	0·016	18	0·29	0·20	0·0032

In column 1 of Table 4 are listed the meteorites in order of increasing depth, divided into three groups rather arbitrarily by their Cl^{36} activity in column 2. It will be noticed that the observed Cl^{36} activity for Casas Grandes has been ignored. The Cl^{36} value in this meteorite does not fall into the general scheme. One possibility is that the meteorite has been on the earth long enough for the Cl^{36} to have decayed. Another possibility is that the chip measured was not representative of the sample used for the Cl^{36}. Column 3 gives the Ar^{38}/Cl^{36} production ratio in meteorites. This value is determined from an Ar^{38}/Ar^{36} ratio of 8 in high energy

bombardments, and a value for the same ratio of 1·6 in meteorites. (In meteorites, the ratio measured as Ar^{38}/Ar^{36} is actually $Ar^{38}/Ar^{36} - Cl^{36}$.) Table 2 shows that this ratio does not vary with energy over the energies considered here, and so we have assumed a constant value at all depths. From these values the Ar^{38} production rate is calculated in column 4. From the He^3/Ar^{38} and Ne^{21}/Ar^{38} ratios we calculate production rates for He^3 and Ne^{21}, respectively. These are listed in columns 6 and 8. The He^3/Ar^{38} and Ne^{21}/Ar^{38} ratios are average values for each group of meteorites as defined in the table. In calculating these average values, anomalous ratios were disregarded. The exposure ages calculated from these values and from the total isotopic abundances are given in Table 5. These ages are expected to be correct to within a factor of 2. Further Cl^{36} determinations should improve the accuracy of this method.

An anomalous content for any nuclide will result in a false age estimate. Thus Tucson, with a high Ne^{21} content, gives a misleadingly high Ne^{21} exposure age. In column 11 of Table 5 are listed average exposure ages for each meteorite. The exposure ages calculated for the three isotopes He^3, Ne^{21}, and Ar^{38}, are in good agreement with each other and with the Cl^{36}–Ar^{36} values, which are also listed. By using three isotopes it is easy to pick out the values which are probably influenced by impurities. In deciding on an average age, all such anomalous ages were disregarded.

No exposure ages have been calculated for Tombigbee River. The ratios for this meteorite are so far removed from the others that a production rate based on the Cl^{36} numbers would not be valid.

Conclusions

The exposure ages estimated in this paper are a different type of age from that indicated by uranium–helium, lead–lead, or potassium–argon dating procedures. These latter ages measure the time of formation or solidification of the meteorites or parent body, while the exposure ages measure the time since formation of the fragments which actually arrived on the earth.

The spread in exposure ages estimated above indicates that there was no one cataclysmic event which produced all the meteorites. This does not preclude the possibility of the break-up of a body or bodies of planetary or lunar dimensions as the origin of meteorites. If this is the manner of formation assumed, however, the spread in ages does indicate that the original break-up must have formed fragments larger than the meteorites, and that these large fragments are then broken up by a continuous process of collisions among themselves. If it is assumed that the meteorites are rather the remains from the formation of the planets, then again these remains must at one time have formed pieces of matter larger than the meteorites, these pieces being broken up over a range of time.

The longest exposure age obtained is an upper limit to the date of the original catastrophe or formation. Thus the Williamstown meteorite indicates that meteorite formation began at least 1700 million years ago. The shortest age, 19 million years for Tucson, indicates that meteorite formation was still taking place at this comparatively recent date. Calculations have been performed (Opik, 1951) which lead to a mean life expectancy for particles of meteoritic dimensions

Table 5. Cosmic-ray exposure ages

Meteorite	He^3 prod. rate[1]	He^3 content[2]	He^3 age (my)	Ar^{38} prod. rate	Ar^{38} content	Ar^{38} age	Ne^{21} prod. rate	Ne^{21} content	Ne^{21} age (my)	Ave. age	Ar^{36} content	Cl^{36} (d/m-kg)	Ar^{36}/Cl^{36} age
Toluca	1·2	100	83	0·031	2·4	78	0·0096	0·8	83	81			
Casas Grandes	1·2	130	108	0·031	3·6	115	0·0096	1·0	104	109			
Arispe	0·70	270	390	0·027	8·9	330	0·0068	2·3	340	350			
Odessa	0·70	220	310	0·027	12	450	0·0068	2·3	340	325	7	7·8	370
Sikhote Alin	0·70	130	185	0·027	4·1	150	0·0068	1·5	220	165	2·8	6·9	170
Washington Co.	0·70	193	275	0·027	7·5	280	0·0068	2·06	300	285			
Tucson	0·70	13	19	0·027	0·53	20	0·0068	0·81	120	20			
Forsyth Co.	0·70	48	70	0·027	2·1	80	0·0068	0·58	85	75			
Canon Diablo	0·70	95	135	0·027	4·3	160	0·0068	0·97	140	145	2·7	6·8	160
Smithland	0·70	58	86	0·027	2·6	96	0·0068	0·62	91	90			
Williamstown	0·29	480	1700	0·016	264	1600	0·0032	6·0	1870	1720	17·4	3·3	2200
Santa Rosa	0·29	47	160	0·016	2·3	140	0·0032	0·44	140	140			
Santa Catherina	0·29	57	200	0·016	2·8	170	0·0032	0·52	162	166			
Carbo	0·29	350	1200	0·016	18	1100	0·0032			1100	11	3·6	1200

[1] Units for production rates are 10^{-4} scc/g-my.
[2] Units for contents are 10^{-4} scc/g.

crossing the orbit of the earth of approximately 100–300 million years. Thus exposure ages would be expected to cluster around this value. The ages obtained in this paper are not inconsistent with these calculations.

Appendix

Description of Meteorites (Prior *and* Hey, 1953)

Forsyth County is a nickel-poor ataxite, found about 1891 in Forsyth County, North Carolina. One mass of about 50 lb, it contains 5·55 per cent nickel. The piece used in this research was obtained from Dr. Brian Mason of the American Museum of Natural History.

Santa Catherina is a nickel-rich ataxite found in 1875 in Brazil. Large masses totaling about 7000 kg were found in clay overlying granite. Total weight may have been as much as 25,000 kg. There was some previous doubt as to its origin, but the present investigation confirms this as meteoritic by the observed abundance of such isotopes as helium-3 and neon-21. It contains 33·97 per cent nickel. The specimen used was obtained from Dr. E. L. Fireman, of the Smithsonian Astrophysical Laboratory of the Harvard Observatory.

Santa Rosa has a structure listed as ataxite to obscure brecciated octahedrite. It was found in 1810 in Columbia and contains about 6·7 per cent nickel. It consists of a large mass of 750 kg and several smaller pieces. The specimen used was obtained through the courtesy of Dr. Mason.

Smithland was found in 1839–40 in Kentucky. It is a nickel-rich ataxite, with 16·4 per cent nickel. A large mass was found and partly smelted; 5 kg remain. The specimen used was obtained through the courtesy of Dr. Fireman.

Tombigbee River was found in 1859 in Alabama. It is a nickel-poor ataxite, with 4·1 per cent nickel. Six masses, total weight about 96 lb, were found from 1859 to 1886. The specimen used here was obtained through the courtesy of Dr. Mason.

Tucson consists of two large masses, one ring-shaped weighing 688 kg and the other weighing 287 kg. The masses have been known for centuries and were transported to Tucson, Arizona from a point some 30 miles further south. This specimen was from the 287 kg meteorite, an ataxite of 8·9 per cent nickel. The ring has 9·2 per cent nickel. The specimen was obtained through the courtesy of Dr. Fireman.

Washington County, a nickel-rich ataxite, was found in 1927 in Colorado. It appeared to be a fresh disk-shaped mass, and there was considerable doubt as to its origin, which has been settled by the helium-3 and neon-21 abundances as meteoritic. It contains 9·3 per cent nickel. The specimen used in this research was obtained through the courtesy of Dr. E. L. Fireman.

Canon Diablo, no. 34·3767, is a medium octahedrite found in Arizona in 1891. It consists of many fragments ranging from minute pieces to pieces weighing over 1000 lb. The total mass is over 30 tons. It contains 7·17 per cent nickel. The specimen used was obtained from Ward's Natural Science Establishment, Rochester, New York.

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References

Arrol W. J., Jacobi R. B. and Paneth F. A. (1942) Meteorites and the age of the solar system. *Nature, Lond.* **149,** 235–238.

Bauer C. A. (1947) Production of helium in meteorites by cosmic radiation. *Phys. Rev.* **72,** 354–355.

Bauer C. A. (1948a) The absorption of cosmic radiation in meteorites. *Phys. Rev.* **74,** 225–226.

Bauer C. A. (1948b) Rate of production of helium in meteorites by cosmic radiation. *Phys. Rev.* **74,** 501–503.

Begemann F., Geiss J. and Hess D. C. (1957) Radiation age of a meteorite from cosmic ray produced He^3 and H^3. *Phys. Rev.* **107,** 540–542.

Ebert K. H. and Wänke H. (1957) Uber die Einwirkung der Hohenstrahlung auf Eisenmeteorite. *Z. Naturf.* **12a,** 766–773.

Fechtig H., Gentner W. and Kistner G. (1960) Raumliche Verteilung der Edelgasisotope im Eisenmeteoriten Treysa. *Geochim. et Cosmochim. Acta.* To be published.

Fireman E. L. and Defelice J. (1960) Argon-39 and tritium in meteorites. *Geochim. et Cosmochim. Acta* **18,** 183–192.

Fireman E. L. and Schwarzer D. (1957) Measurement of Li^6, He^3, and H^3 in meteorites and its relation to cosmic radiation. *Geochim. et Cosmochim. Acta* **11,** 252–262.

Fireman E. L. and Zähringer J. (1957) Depth variation of tritium and argon-37 produced by high-energy protons in iron. *Phys. Rev.* **107,** 1695–1698.

Gentner W. and Zähringer J. (1957) Argon und Helium als Kernreaktionsproducte in Meteoriten. *Geochim. et Cosmochim. Acta* **11,** 60–71.

Gerling E. K. and Levskii L. K. (1958) Cosmic Radiation products in the Sikhote Alin meteorite. *Soviet Phys., J.E.T.P.* **3,** 1082–1085.

Hoffman J. H. and Nier A. O. (1958) Production of helium in iron meteorites by the action of cosmic rays. *Phys. Rev.* **112,** 2112–2117.

Hoffman J. H. and Nier A. O. (1959) The cosmogenic He^3 and He^4 distribution in the meteorite Carbo. *Geochim. et Cosmochim. Acta* **17,** 32–36.

Huntley H. E. (1948) Production of helium by cosmic rays. *Nature, Lond.* **161,** 356.

Kuznetsov V. V. and Mekhedov V. N. (1959) Tritium production in metals by 120 to 660-meV protons. *Soviet Phys., J.E.T.P.* **35,** (8), No. 3, 406–409. Translation.

Neher H. V. (1958) The primary cosmic radiation. *Ann. Rev. Nuc. Sci.* **8,** 217–242.

Opik E. J. (1951) Collision probabilities with the planets and the distribution of inter-planetary matter. *Proc. Roy. Irish Acad.* **54,** 165–200.

Paneth F. A., Reasbeck P. and Mayne K. I. (1953) Production by cosmic rays of helium-3 in meteorites. *Nature, Lond.* **172,** 200–201.

Prior G. T. and Hey M. H. (1953) *Catalogue of Meteorites.* William Cloves, London.

Reasbeck P. and Mayne K. I. (1955) Cosmic radiation effects in meteorites. *Nature, Lond.* **176,** 733–734.

Schaeffer O. A. and Fisher D. E. (1959) Cosmogenic noble gases in the Washington County meteorite. *Nature, Lond.* **183,** 660–661.

Schaeffer O. A. and Zähringer J. (1959) High sensitivity mass spectrometric measurement of stable helium and argon isotopes produced by high energy protons in iron. *Phys. Rev.* **113,** 674–678.

Schaeffer O. A. and Zähringer J. (1960) Helium, neon and argon isotopes in some iron meteorites. *Geochim. et Cosmochim. Acta.* **19,** 94–99.

Schaeffer O. A. (1959) *High sensitivity Mass Spectrometry of the Rare Gases.* Brookhaven National Laboratory Report, BNL 581. Unpublished.

Singer S. F. (1958) Cosmic-ray evidence on the origin of meteorites. *Nuovo Cim.* **8,** 539–548.

Sprenkel E. L. (1959) *Cosmic-ray produced chlorine-36 activities in iron meteorites.* (Unpublished) thesis.

Urey H. C. (1955) Origin and age of meteorites. *Nature, Lond.* **175,** 321–323.

Urey H. C. (1959) Primary and Secondary objects. *J. Geophys. Res.* **64,** 1721–1739.

Geochimica et Cosmochimica Acta, 1960, Vol. 20, pp. 15 to 29. Pergamon Press Ltd. Printed in Northern Ireland

Adsorption of non-ionic aliphatic molecules from aqueous solutions on montmorillonite. Clay–organic studies—II*†

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Abstract—A series of nonionic aliphatic compounds was adsorbed from aqueous solutions on Ca-montmorillonite and the adsorption isotherms were determined. The differences in molar adsorption are attributed to the influence of the chain length and the CH-activity. These effects are shown to operate independently.

The (001) spacings of the clay-organic complexes were measured and one-, two- and three-layer complexes were recorded. The orientation of the molecules in the one-layer complexes is discussed. It is considered that aliphatic molecules orient with the plane of their chain both parallel and perpendicular to the clay surface.

Introduction

Clay–organic complexes have been the subject of many studies. Most of them, however, deal with the properties and changes in properties of the formed complexes and relatively little attention has been given to the formation process and to the adsorption equilibria in aqueous solutions.

Montmorillonite forms complexes with organic substances either by a cation exchange reaction or by adsorption or both together. The exchange reaction of amine salts was studied by Smith (1934) who first gave adsorption isotherms for salts of nicotine, strychnine, piperidine, amylamine, diamylamine, ammonia and hydrazine. Further adsorption isotherms for octadecylammoniumchloride and dodecylammoniumchloride are given by Jordan (1949). Grim and co-workers (1947) describe the exchange reaction with salts of butylamine, dodecylamine and ethyldimethyldodecylamine; the latter two are adsorbed considerably beyond the exchange capacity of the clay mineral. Cowan and White (1958) present adsorption isotherms of a series of ammonium salts of the type $CH_3-(CH_2)_n-NH_4^+$ in which n goes from 1 to 13. They also find an excess adsorption with $n > 7$. They confirmed Grim's observation that excess adsorption is connected with a decrease in pH, which means that the excess organic material is adsorbed as free amine, $R-NH_2$, and not in the ionic salt form, $R-NH_3^+Cl^-$.

The conclusion may be drawn that neutral molecules are adsorbed on montmorillonite from aqueous solutions only if their molecular size is large enough. Brindley and Rustom (1958) studied the adsorption of a large-sized neutral molecule, the monoester of polyethyleneglycol and oleic acid, and found a smooth isotherm of Langmuir-type similar to that obtained by Greenland (1956) for methylated glucose. Greenland demonstrates that glucose itself shows only a very weak adsorption. This points to the adsorption behaviour being determined

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† Part I see Brindley and Rustom (1958).

not only by the *size* of the molecule, but even more by its *chemical character*. As little is known of the role which the chemical character of an organic molecule plays in the adsorption process, the present studies were designed to obtain more information in this direction.

Neutral organic molecules were selected for the present investigations in order to study the adsorption process uninfluenced by an exchange reaction. The following structural classes of aliphatic compounds were considered: Nitriles, ketones, ester, ether and alcohols. The choice of materials, however, was restricted by the conditions that the molecules should have a minimum chain length of five carbon atoms, and also be water soluble.

Experimental

I. *Materials*

1. *Organic*

The following substances were used: Acetylacetone, Eastman 1088, twice redistilled, b.p. 60°C/60 mm Hg. α-Methoxyacetylacetone, commercial quality, twice redistilled, b.p. 74°C/15 mm Hg. Acetoeaceticethylester, commercial quality, twice redistilled, b.p. 78–81°C/16 mm Hg. Nonanetrione-2:5:8*, m.p. 55°C. Hexanedione-2:5, Aldrich Chemicals, twice redistilled, b.p. 82·5°C/17 mm Hg. β:β'-Oxydipropionitrile, Eastman "practical" grade, twice redistilled, b.p. 156·5–157°C/6 mm Hg. β-Ethoxypropionitrile, American Cyanamid Co., once redistilled, b.p. 70–70·5°C/17·5 mm Hg. Bis-(2-ethoxyethyl)-ether, Fisher Scientific Co., "highest purity" grade, b.p. 76–77·5°C/13 mm Hg (had a slight peroxide content). Bis-(2-methoxyethyl)-ether, Eastman "practical" grade, once distilled with precautions, b.p. 64–65°C/18 mm Hg (had then still a slight peroxide content). Ethyleneglycoldiglycidether, from Chemische Werke Huels, Marl, Germany, redistilled twice, the fraction of 120–123°C/5·5 mm Hg was used. Triethyleneglycol, Fisher Scientific Co., "purified" grade, twice redistilled, b.p. 166°C/16 mm Hg, Diethyleneglycol, Fisher Scientific Co., "reagent" grade, b.p. 129–130°C/10 mm Hg. Triethyleneglycoldiacetate, Eastman "highest purity" grade, b.p. 154–156°C/8 mm Hg. Diethyleneglycoldiacetate, Eastman "highest purity" grade, m.p. 19–20°C. Hexanediol-1:6, Eastman "highest purity" grade, m.p. 42–43°C. Pentanediol-1:5, Eastman "practical" grade, once redistilled, b.p. 131–133°C/12 mm Hg. 2:4-Hexadiynediol-1:6, prepared according to Reppe (1955), m.p. 112–113°C.

2. *Clay material*

A purified Wyoming bentonite, as used in the previous work by Brindley and Rustom (1958), has been used in the present work.

Conversion into the Ca-saturated form: one part bentonite is mixed with fifteen parts water and subsequently with five parts 1 N $CaCl_2$ solution. After standing and centrifuging, it is five times leached with ten parts 1 N $CaCl_2$ solution. Excess $CaCl_2$ is washed out the same way (usually six to seven washings). During the last washings, heavier impurities settle out at the bottom of the centrifuge glass and are removed.

* Prepared on the basis of methods described by Alder and Schmidt (1943).

II. *Experimental Procedure*

1. *Clay–organic interaction*

The experiments were designed completely on a volumetric basis. A standard suspension of Ca-montmorillonite was prepared with a concentration of 30 mg/ml related to Ca-montmorillonite dried at 110°C. Aqueous solutions of the organic materials were set up, usually with the following concentrations: 1000, 500, 200, 100, 50, 20, 10 m-moles/l. A mixture is made of 10 ml of clay suspension and 10 ml of organic solutions. After 20 hr standing, the mixture is centrifuged* in stoppered centrifuge tubes and the supernatant liquid is subsequently carefully decanted. The remaining concentration is then determined by analytical methods.

2. *Analytical procedures*

It would be preferable to determine the organic content by a physical or physicochemical method. It was found that the organic solutions still contained a very faint turbidity of clay which would disturb considerably any spectrophotometric method. The decrease in concentration by adsorption is frequently very small. Therefore the accuracy of the analytical method should be at least ± 1 per cent in order to obtain reasonable values for the amount adsorbed. Consequently, a more time consuming chemical analysis was developed. The determination method was calibrated for each substance usually in the concentration ranges of 0–10 m-moles/l. and 20–50 m-moles/l. Aliquots of higher concentrated samples were taken to bring them into these concentration ranges.

(a) *Saponification reactions*

Determination of acetoaceticethylester. After Skrabal and Zahorka (1925) acetoaceticester can be saponified quantitatively if only a slight excess of NaOH is used. They find that a 4 hr reaction period at room temperature is the most favourable; the reaction is then almost complete and unwanted side reactions have not yet become of too great influence. The present experiments revealed a marked dependence on the reaction time but the results were well reproducible if titrated back against phenolphthaleine after exactly the same time (4 hr).

Analysis for samples in the concentration range 20–50 m-moles/l.: 15 ml 0·05 N NaOH + 10 ml sample solution titrated back after exactly 4 hr with 0·03 N HCl. For the concentration range 0–10 m-moles/l.: 15 ml 0·01 N NaOH + 10 ml sample, titrated with 0·01 N HCl.

Determination of diethyleneglycoldiacetate and triethyleneglycoldiacetate. The same method of alkaline saponification at room temperature proved to be satisfactory also for diethyleneglycoldiacetate and triethyleneglycoldiacetate.

Concentration range 20–50 m-moles/l.: 15 ml 0·1 N NaOH + 10 ml sample, titrated after 4 hr with 0·05 N HCl against phenolphthaleine: concentration range 0–10 m-moles/l.: 15 ml 0·02 N NaOH + 10 ml sample, titrated with 0·01 N HCl.

(b) *Oximation reactions*

Reaction with hydroxylamine was used to determine all the ketones. Two different methods were applied, the one oximation with free hydroxylamine in

* It should be mentioned that the temperature in the centrifuge rose to 40–45°C especially when long centrifuging times were required.

aqueous ethanol, according to Torozzolo and Lieber (1950), the other oximation with hydroxylaminehydrochloride in water. The first pushes the oximation equilibrium farther towards the oxime, therefore nonanetrione-2:5:8 forms a dioxime or even a slight amount of trioxime, hexanedione-2:5 forms the dioxime. Oximation with hydroxylaminehydrochloride in water forms free HCl which in turn reverses the reaction, and the equilibrium is not completely at the side of the oxime. This results in the formation of the dioxime for the nonanetrione-2:5:8 and of the monoxime for the hexanedione-2:5. The titration of the formed HCl shifts the equilibrium and precludes accurate determination of the end point with small excesses of $NH_2OH \cdot HCl$. The reaction of hydroxylamine with 1:3-diketones forms the monoxime, probably followed by a ring closure to the corresponding isoxazole.

Determination of nonanetrione-2:5:8. Concentration range 20–50 m-moles/l.: 50 ml 0·1 N $NH_2OH \cdot HCl$ + 10 ml sample titrated after 30 min with 0·05 N NaOH against bromophenol-blue. Concentration range 0–10 m-moles/l.: 10 ml 0·1 N $NH_2OH \cdot HCl$ + 10 ml sample titrated with 0·01 N NaOH.

Determination of hexanedione-2:5. Concentration range 20–50 m-moles/l.: 10 ml sample treated according to Torozzolo and Lieber (1950). Concentration range 0–10 m-moles/l.: as for nonanetrione-2:5:8.

Determination of α-methoxyacetylacetone. Concentration range 20–50 m-moles/l.: 25 ml 0·1 N $NH_2OH \cdot HCl$ + 10 ml sample titrated after 40 min with 0·02 N NaOH against bromophenol-blue. Concentration range 0–10 m-moles/l.: as for nonanetrione-2:5:8 with 40 min reaction time.

Determination of acetylacetone. Concentration range 20–50 m-moles/l.: 10 ml sample treated according to Torozzolo and Lieber (1950). Concentration range 100–125 m-moles/l.: 25 ml 0·1 N $NH_2OH \cdot HCl$ + 10 ml sample titrated after 40 min with 0·1 N NaOH against bromophenol-blue.

(c) *Oxidation reactions*

Oxidation with potassium dichromate in dilute sulphuric acid, the so-called "wet combustion method", was applied to all the other compounds, including also acetylacetone and ethyleneglycoldiglycidether. A detailed description of the different aspects and procedures of this method will be published elsewhere (see Hoffmann).

(d) *Special methods*

Ethyleneglycoldiglycidether was subjected to two determination methods, wet combustion and reaction with sodium thiosulphate. The latter is described by Ross (1950) and was applied to one 10 ml sample in the concentration range 20–50 m-moles/l.

3. *X-ray analysis*

The clay remaining in the centrifuge tube (see 1) was wetted with a few drops of water; a sample of the resulting paste was placed on a glass slide and allowed to dry in a desiccator over P_2O_5. The drying temperature was kept below 25°C (during summer in a refrigerator) because higher temperatures decrease the drying

efficiency of the P_2O_5 and result in incomplete drying. The X-ray patterns are taken under a stream of air dried first over a column of Linde molecular sieve A4, and subsequently over P_2O_5 cooled in an ice bath.

The X-ray patterns were recorded by a Philips Norelco diffractometer with Cu K_α radiation at 40 kV, 15 mA. The limitations of this technique will be discussed in the last part of this paper (see Discussion, Section II, 1).

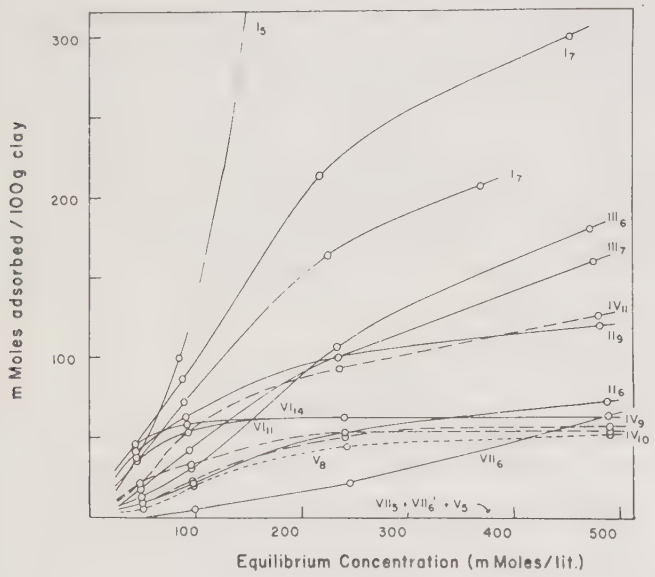


Fig. 1. Apparent adsorption isotherms for adsorption of aliphatic compounds from aqueous solutions on Ca-montmorillonite.

Results

I. *Adsorption isotherms**

The observed depletions in concentrations are presented in Table 1. These values are converted to millimoles adsorbed per 100 g clay and plotted against the equilibrium concentration in Fig. 1, where the Roman figures characterize the chemical character and the Arabic figures the chain lengths of the organic molecules. The rather large experimental errors for the amounts adsorbed are due to the fact that they represent small changes of comparatively large concentrations. The accuracy of the analytical methods is about ± 1 per cent or less (in a few cases ± 2 per cent) of the absolute amount. If the adsorption causes a concentration depletion of only 5 per cent of the surrounding solution, it is easily seen that this results in a 20 per cent error in the amount adsorbed. The limits stated in Table 1 are based on the reproducibility of the results for the particular analytical method used. At present, there seems to be no possibility of determining directly the amount adsorbed on the clay while in equilibrium with the solution. Other possible errors arise from the frequent handling, centrifuging, pipetting and diluting of the solutions. The values found for diethyleneglycol or 2:4-hexadiynediol-1:6 provide an excellent check in this direction, as they are not adsorbed: The maximum deviation found was 0·5 per cent of the theoretical value.

* It should be recognized that the curves in this paper are composite adsorption isotherms representing the adsorption equilibrium of the organic substance and water.

Table 1. Concentration depletion by adsorption (m-moles/l.)

Material \ Initial conc. (m-moles/l.)	5	10	25	50	100	250	500
Acetylacetone	0·4 ± 0·1	0·8 ± 0·2	2·0 ± 1·0	6·2 ± 1·0	15 ± 2	49 ± 4	137 ± 8
α-Methoxyacetylacetone	0·7 ± 0·1	2·6 ± 0·1	4·2 ± 0·2	6·9 ± 0·5	12·9 ± 0·7	32 ± 2	45 ± 4
Acetoaceticethylester	1·2 ± 0·05	1·4 ± 0·1	2·8 ± 0·1	5·1 ± 0·3	10·8 ± 0·6	24·6 ± 1	31 ± 3*
Nonanetrione-2:5:8	—	1·4 ± 0·1	2·7 ± 0·2	5·8 ± 0·3	9·5 ± 0·6	15 ± 2	18 ± 4
Hexanedione-2:5	0·2 ± 0·1	0·6 ± 0·1	0·7 ± 0·5	1·4 ± 0·7	3·3 ± 1	8 ± 3	11 ± 5
β:β′-Oxydipropionitrile	0·2 ± 0·1	0·2 ± 0·1	0·8 ± 0·2	2·7 ± 0·3	6·2 ± 0·5	15 ± 1·5	24 ± 3
β-Ethoxypropionitrile	—	0·2 ± 0·1	0·9 ± 0·1	2·0 ± 0·3	4·6 ± 0·5	16 ± 1·5	27 ± 3
Bis-(2-ethoxyethyl)-ether	0·3 ± 0·1	0·3 ± 0·1	1·4 ± 0·2	3·3 ± 0·3	8·1 ± 0·6	14 ± 1·5	19 ± 3
Bis-(2-methoxyethyl)-ether	—	0 ± 0·1	0·7 ± 0·1	1·5 ± 0·3	3·5 ± 0·6	7·6 ± 1·5	8·7 ± 3
Ethyleneglycoldiglycidether	0·3 ± 0·1	0·7 ± 0·1	1·6 ± 0·1	3·2 ± 0·3	4·9 ± 0·6	8·2 ± 1·5	6·3 ± 3
Triethyleneglycol	—	-	0·4 ± 0·1	0·9 ± 0·2	3·5 ± 0·5	6·7 ± 1·2	7·9 ± 2·5
Diethyleneglycol	—	—	+0·1 ± 0·2	0·3 ± 0·5	0 ± 0·6	0·5 ± 1·5	0 ± 3
Triethyleneglycoldiacetate	1·0 ± 0·1	1·8 ± 0·1	4·1 ± 0·2	6·8 ± 0·3	8·7 ± 0·6	9·5 ± 1·5	6·0 ± 3
Diethyleneglycoldiacetate	0·8 ± 0·1	1·3 ± 0·1	2·8 ± 0·2	5·3 ± 0·3	7·9 ± 0·6	9·3 ± 1·5	8·5 ± 3
Hexanediol-1:6	—	—	−0·6 ± 0·3	0·1 ± 0·3	0·8 ± 0·6	3·3 ± 1·5	9·5 ± 3
Pentanediol-1:5	—	—	0·1 ± 0·2	0·7 ± 0·5	0·4 ± 0·6	0·1 ± 1·5	0·3 ± 3
2:4-Hexadiynediol-1:6	—	—	0 ± 0·1	0 ± 0·3	−0·1 ± 0·6	+0·6 ± 1·0†	

* Initial conc. = 400.
† Initial conc. = 200.

The adsorption isotherms shown in Fig. 1 vary in initial slope and in maximum molar adsorption. The 1:3-diketones and the acetoaceticethylester show the highest molar adsorption followed by the nitriles, nonanetrione-2:5:8 and bis-(2-ethoxyethyl)-ether. Steep initial slope and early saturation are found for the polyethyleneglycoldiacetates. Small slope and a gradual approach to saturation are represented by hexanedione-2:5, bis-(2-methoxyethyl)-ether, ethyleneglycoldiglycidether and triethyleneglycol. Hexanediol-1:6 is barely adsorbed, and diethyleneglycol, pentanediol-1:5 and 2:4-hexadiynediol-1:6 are not adsorbed at all. Many of the curves have a slight S-shape, and only nonanetrione-2:5:8 approximates to a Langmuir isotherm.

The physical behaviour of the clay–organic mixtures gives some hint as to the extent of molar adsorption. Mixtures with high molar adsorption tend to form gels and to stay in suspension and they require longer centrifuging times (from 10 to 20 hr). Mixtures with low molar adsorption settle out on standing and require only a 2 hr centrifugation period.

II. *X-ray data*

There is a marked tendency for Ca-montmorillonite to form regular complexes or mixtures thereof with the tested substances in preference to intermediate structures. The different complexes are formed in a regular sequence corresponding to increasing concentration of organic material in the solution. The recorded spacings are given in Table 2. They are the mean of several samples of the same type and include the standard deviations.

With little or no organic material present, a spacing of 11·7–12·1 Å is obtained. This compares with the 11·7 Å complex of pure Ca-montmorillonite formed under the same drying conditions. This spacing is due to residual water as gentle heat treatment leads to the fully collapsed Ca-montmorillonite with a spacing of 9·5 Å. This type of complex is not considered further.

The spacings of the one-layer complexes vary within 13·0–13·4 Å, apart from the higher values for pentanediol-1:5 and hexanediol-1:6.

The two-layer complexes lie within 16·5–17·5 Å, apart from 2:4-hexadiynediol-1:6, diethyleneglycol and β:β'-oxydipropionitrile, which give smaller two-layer spacings. The latter two substances form additional complexes with higher spacings; the three-layer complex of β:β'-oxydipropionitrile with 20·4 Å. Ca-montmorillonite immersed in diethyleneglycol gives a 16·9 Å spacing which after drying diminishes to 15·6 Å.

It was found that washing the clay paste before drying very easily removes the organic content. Gentle washing after drying (e.g. immersion for 8 hr in water) takes the organic content completely out of any complex of pentanediol-1:5, hexanediol-1:6 or β:β'-oxydipropionitrile.

Discussion

I. *Adsorption isotherms*

1. *Influence of chain length.* In Fig. 1 the substances are characterized according to chemical character and chain length. All the molecules studied have straight chains. Therefore steric factors can be neglected. To demonstrate the

influence of the chain length, several samples of the same chemical character are taken from Fig. 1 and are presented in Fig. 2. In agreement with observations by Grim and co-workers (1947) and by Cowan and White (1958), the molar adsorption increases with increasing chain length. For example, pentanediol-1:5 is not adsorbed from aqueous solutions, but extension by one CH_2-group leads to the weak adsorption of hexanediol-1:6. A similar effect is observed in the group of the polyethyleneglycols (Group V). Within the group of the ethers (Group IV), adsorption increases slightly in going from bis-(2-methoxyethyl)-ether with a

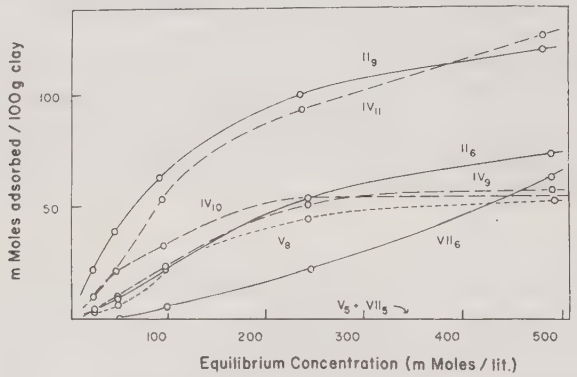


Fig. 2. Influence of the chain length on molar adsorption.

chain length of nine units to bis-(2-ethoxyethyl)-ether with a chain length of eleven units. The curve for ethyleneglycoldiglycidether having a slightly different chemical character and a chain length of ten units lies in between. A marked increase is observed in the group of 1:4-diketones (Group II), where a change of three units in chain length between hexanedione-2:5 and nonanetrione-2:5:8 causes a marked increase in adsorption.

It is concluded that a chain length of from five to six units is necessary to start adsorption from aqueous solution. The chain length has a strong influence up to about ten units, but beyond this point differences in chain length seem not to affect the adsorption very appreciably. This is demonstrated by the groups of the ethers (Group IV) and especially by the group of the polyethyleneglycoldiacetates (Group VI, Fig. 1). If a molecule is large enough to establish adsorption, the adsorption behaviour is then determined mainly by the chemical character.

2. *Influence of chemical character.* The main emphasis of the present work was to evaluate chemical features affecting adsorption. Among earlier investigations, Haxaire and Bloch (1956) tried to correlate the number of π-electrons and the molecular thickness with the amount adsorbed. Talibudeen (1955) presented a correlation between molar volume, amount exchanged, the number of cationic groups per molecule, and the observed spacing. Barshad (1952) studied the influence of the dielectric constant as well as that of the dipole moment of the adsorbed molecules on what complexes are formed. MacEwan and Talibudeen (1949) demonstrated the influence of activated methylene groups on the spacings of one-layer complexes with halloysite. MacEwan (1948) gave a good description of this activation by neighbouring electron-withdrawing groups, which is also

called CH-activity and will be referred to as such in the present paper. At an early date, BRADLEY (1945) concluded that the adsorbed molecules are held not so much by hydrogen bonding of the O—H · · · O—Si or N—H · · · O—Si type, as by a kind of hydrogen bonding over the methylene groups of the aliphatic chain, thus forming a C—H · · · O—Si interaction as only this bond shows an appreciable contraction. If this theory, which was also applied by MACEWAN (1948), holds true, differences in CH-activity of molecules should lead to different adsorption patterns. In the present work, the organic substances were chosen with these ideas in mind.

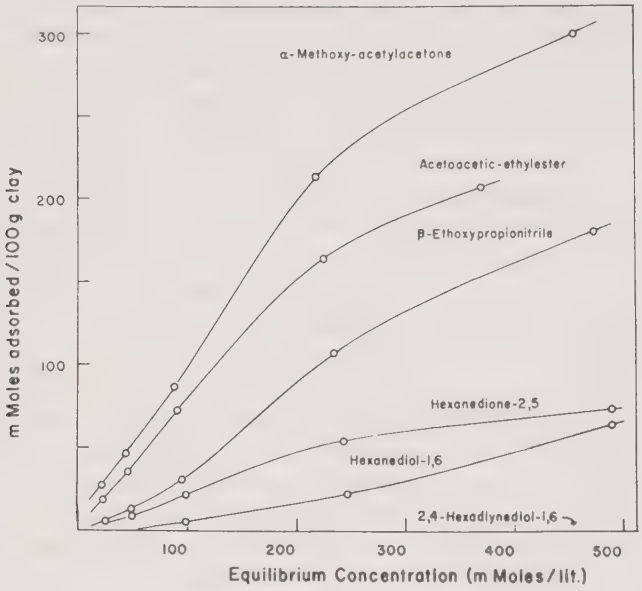


Fig. 3. Influence of chemical character on molar adsorption with a constant chain length from six to seven units.

The effect of change in chemical character with a nearly constant chain length (from six to seven units) is shown in Fig. 3. The sequence 2:4-hexadiynediol-1:6, hexanediol-1:6, hexanedione-2:5, β-ethoxypropionitrile, acetoaceticethylester, α-methoxyacetylacetone clearly shows that increasing CH-activity leads to higher molar adsorption. The methylene group in 1:3-diketones and β-ketoester is more active than the α-methylene group in nitriles, which in turn is more active than the methylene groups in 1:4-diketones, while the methylene groups in ether and alcohols are only slightly active. 2:4-Hexadiynediol-1:6 has eight hydrogen atoms less than hexanediol-1:6; this accounts for the comparatively weaker molar adsorption of the former. When differences in chain length are taken into consideration, the other compounds of Fig. 1 fit into the general picture.

When considering CH-activity as an important factor of adsorption, it should also be kept in mind that CH-activity causes the formation of an enol in the case of the 1:3-diketones, which might be the adsorbed species. Furthermore, CH-activity cannot be divorced from the polarity by which it is induced. But if

polarity were the determining factor, the nitriles—their dipole moment μ can be estimated to be 3·5–4·0 D—ought to show the highest molar adsorption (for 1:3-diketones, $\mu = 3{\cdot}0$ D) whereas bis-(2-ethoxyethyl)-ether with $\mu = 2{\cdot}0$ D should be less adsorbed than diethyleneglycol and the tested diols with $\mu \simeq 2{\cdot}5$ D. With regard to this and to Bradley's theory and its consistency with other reported observations, the present writers prefer to relate the differences in adsorption to the influence of the CH-activity.

The two main factors which influence adsorption, namely chain length and CH-activity, appear to operate independently. For example, pentanediol-1:5 with a chain length of five units is not adsorbed, while acetylacetone with the same chain length but with strong CH-activity is highly adsorbed. On the other hand a lack of CH-activity can be overcome by higher chain length, which is demonstrated by the pair diethyleneglycol-triethyleneglycol.

3. *Influence of side reactions.* Cation exchange reactions could occur, if the organic molecule were able to form cations. Only the 1:3-diketones can provide a dissociable proton in strong alkaline medium. In view of the extremely small acidity of these compounds, an exchange reaction is rather unlikely.

The 1:3-diketones could be considered to form complexes in the enol form, with the exchangeable cations between the clay sheets but since no break is found in the absorption curve corresponding to the number of cations, complex formation of this kind probably plays no major role.

It was observed that the clay–organic mixtures of the 1:3-diketones turned increasingly brownish with increasing concentration. This may be due to an intermolecular condensation, catalysed by the negatively charged clay surface. As the oximation analysis—which determines the number of keto groups—in an exploratory test differed very little from the actual analysis made by the wet combustion method—which determines the carbon content—self condensation, if it exists at all, remains restricted to the clay surface.

The hydrolysis of epoxide groups is rather strongly catalysed by anions. Therefore the clay surface could be expected to act as well on ethyleneglycoldiglycidether. Addition of thiosulphate ions to the epoxide groups showed that a sample after contact with Ca-montmorillonite had only 65 per cent of the epoxide groups present compared with an untreated solution of the same age. Thus the clay catalyses the hydrolysis of epoxides.

II. *X-ray measurements*

1. *Limitations affecting their interpretation.* A variety of experimental factors limit the usefulness of the X-ray data. Ca-montmorillonite is very hygroscopic and its hygroscopicity was not diminished by adsorption of the organic substances studied here. The one-layer complexes especially showed a strong tendency to rehydrate rapidly under atmospheric humidity and to assume a spacing of 15·3 Å, the spacing normally taken up by Ca-montmorillonite. The spacings of the two-layer complexes appear less sensitive to atmospheric humidity.

It is necessary to establish as nearly as possible a completely dry atmosphere over the clay–organic sample by having an adequate flow of dry air during X-ray measurements. Under these conditions the (001) spacings of the complexes

appear to be governed essentially by the organic molecules and can be expected to give information concerning molecular orientation. However, the flow of dry air may also cause the organic material to "evaporate" from the clay. Changes in spacings up to 0·3 Å were occasionally found which could have arisen from this cause. These observations confirm the doubts expressed by Grim (1953) concerning the exact meaning of spacings that have been reported without description of the humidity control.

The preparation of completely dry clay–organic complexes with the equilibrium amount of organic material on the clay is impossible to achieve exactly with the organic substances used in this study. Any washing treatment tends to remove the organic materials from the clay and drying without washing treatment inevitably changes the organic content also.

In the case of high-boiling organic substances, the water evaporates preferentially, leaving behind the organic material and the clay which then form a complex corresponding to montmorillonite immersed in an organic liquid. This is evident with diethyleneglycol or pentanediol-1:5 which form well-ordered complexes after drying but were previously not adsorbed from the solution as illustrated by Fig. 1. If the organic substance is comparatively low-boiling, it evaporates together with the water, leaving the pure clay behind. This is demonstrated by acetylacetone from which, by regular drying in a desiccator, complexes could not be obtained despite the high adsorption from aqueous solutions*.

Other complexes lie somewhere between these extremes and are sensitive to loss of organic content according to the boiling point of the organic substance. This applies also to exposure to the open air or to a stream of air.

Therefore the dried complexes may have little in common with adsorption equilibria existing in solution. This precludes any exact correlation between the adsorption data and the type of complex formed. Problems arising from the sequence of complexes and the presence of more than one complex were discussed earlier by Brindley and Rustom (1958).

2. *The layer-spacing data.* The spacings of the one-layer complexes vary within 13·0–13·4 Å with the exception of pentanediol-1:5 and hexanediol-1:6. These different spacings may arise from any or all of the following. Different molecular cross-sections, different shortenings of contact distances, different molecular orientations. Data necessary for a consideration of these various influences are listed in Table 2, columns (3)–(8).

Greene-Kelly (1956), on the basis of X-ray data for cyclic aliphatic compounds, concluded that straight chain aliphatic compounds in general are oriented with the plane of the carbon chain perpendicular to the clay surface, with a contraction of the contact distances up to about 1·0 Å for two clay–organic contacts. In the present work the spacings obtained for the alcohols, diethyleneglycolethers and polyethyleneglycols are in line with the values given by Greene-Kelly. Therefore it may be concluded that these molecules are also oriented with the plane of the

* The spacings for complexes of acetylacetone given in Table 2 are obtained by drying over Linde molecular sieve A4 in an atmosphere saturated with acetylacetone (resulting in a mixture of one- and two-layer complexes).

Table 2. Layer spacings and data relating to molecular orientation

Substance	(1) Observed spacings (Å) One-layer	(2) Observed spacings (Å) Two-layer	(3) Δ_I One-layer spacing −9·50 Å	(4) Calculated thickness of molecules* (Å) oriented ⊥	(5) Calculated thickness of molecules* (Å) oriented ∥	(6) Shortening of contact distances (Å) if oriented ⊥ (4)–(3)	(7) Shortening of contact distances (Å) if oriented ∥ (5)–(3)	(8) Probable orientation
Acetylacetone	$13{\cdot}0_0$	$17{\cdot}1_0$	$3{\cdot}5_0$	$5{\cdot}2_0$	$4{\cdot}1_5$	$1{\cdot}7_0$	$0{\cdot}6_5$	∥
α-Methoxyacetylacetone	$13{\cdot}0_0 \pm 0{\cdot}1_0$	$16{\cdot}9_5 \pm 0{\cdot}1_0$	$3{\cdot}5_0 \pm 0{\cdot}1_0$	$5{\cdot}2_0$	$4{\cdot}1_5$	$1{\cdot}7_0 \pm 0{\cdot}1_0$	$0{\cdot}6_5 \pm 0{\cdot}1_0$	∥
Acetoaceticethylester	$13{\cdot}1_0 \pm 0{\cdot}1_0$	$17{\cdot}1_5 \pm 0{\cdot}1_0$	$3{\cdot}6_0 \pm 0{\cdot}1_0$	$5{\cdot}2_0$	$4{\cdot}1_5$	$1{\cdot}6_0 \pm 0{\cdot}1_0$	$0{\cdot}5_5 \pm 0{\cdot}1_0$	∥
Nonanetrione-2:5:8	$13{\cdot}1_0 \pm 0{\cdot}1_0$	$17{\cdot}3_0 \pm 0{\cdot}1_0$	$3{\cdot}6_0 \pm 0{\cdot}1_0$	$5{\cdot}9_0$	$4{\cdot}1_5$	$2{\cdot}3_0 \pm 0{\cdot}1_0$	$0{\cdot}5_5 \pm 0{\cdot}1_0$	∥
Hexanedione-2:5	$13{\cdot}0_5 \pm 0{\cdot}1_0$	$16{\cdot}8_5 \pm 0{\cdot}1_0$	$3{\cdot}5_5 \pm 0{\cdot}1_0$	$5{\cdot}8_5$	$4{\cdot}1_5$	$2{\cdot}3_0 \pm 0{\cdot}1_0$	$0{\cdot}6_0 \pm 0{\cdot}1_0$	∥
β:β′-Oxydipropionitrile	$13{\cdot}1_5 \pm 0{\cdot}0_5$	$15{\cdot}7_5 \pm 0{\cdot}1_0$	$3{\cdot}6_5 \pm 0{\cdot}0_5$	$4{\cdot}8_5$	$4{\cdot}1_5$	$1{\cdot}2_0 \pm 0{\cdot}0_5$	$0{\cdot}5_0 \pm 0{\cdot}0_5$	∥
β-Ethoxypropionitrile	$13{\cdot}2_5 \pm 0{\cdot}0_5$	—	$3{\cdot}7_5 \pm 0{\cdot}0_5$	$4{\cdot}8_0$	$4{\cdot}1_5$	$1{\cdot}0_5 \pm 0{\cdot}0_5$	$0{\cdot}4_0 \pm 0{\cdot}0_5$	∥?
Bis-(2-ethoxyethyl)-ether	$13{\cdot}4_0 \pm 0{\cdot}2_0$	$16{\cdot}7_5 \pm 0{\cdot}1_0$	$3{\cdot}9_0 \pm 0{\cdot}2_0$	$4{\cdot}5_5$	$4{\cdot}1_5$	$0{\cdot}6_5 \pm 0{\cdot}2_0$	$0{\cdot}2_5 \pm 0{\cdot}2_0$	⊥
Bis-(2-methoxyethyl)-ether	$13{\cdot}2_5 \pm 0{\cdot}1_0$	$17{\cdot}0_0 \pm 0{\cdot}0_5$	$3{\cdot}7_5 \pm 0{\cdot}1_0$	$4{\cdot}5_5$	$4{\cdot}1_5$	$0{\cdot}8_0 \pm 0{\cdot}1_0$	$0{\cdot}4_0 \pm 0{\cdot}1_0$	⊥
Ethyleneglycoldiglycidether	$13{\cdot}4_0 \pm 0{\cdot}1_0$	$17{\cdot}6_0 \pm 0{\cdot}1_0$	$3{\cdot}9_0 \pm 0{\cdot}1_0$	?	?	—	—	—
Triethyleneglycol	$13{\cdot}3_0 \pm 0{\cdot}1_0$	$17{\cdot}3_5 \pm 0{\cdot}0_5$	$3{\cdot}8_0 \pm 0{\cdot}1_0$	$4{\cdot}5_5$	$4{\cdot}1_5$	$0{\cdot}7_5 \pm 0{\cdot}1_0$	$0{\cdot}3_5 \pm 0{\cdot}1_0$	⊥
Diethyleneglycol	$13\ 3_0 \pm 0{\cdot}1_5$	$15{\cdot}7_5 \pm 0{\cdot}1_0$	$3{\cdot}8_0 \pm 0{\cdot}1_5$	$4{\cdot}5_5$	$4{\cdot}1_5$	$0{\cdot}7_5 \pm 0{\cdot}1_5$	$0{\cdot}3_5 \pm 0{\cdot}1_5$	⊥
Triethyleneglycoldiacetate	$13{\cdot}3_5 \pm 0{\cdot}1_5$	$16{\cdot}5_0 \pm 0{\cdot}1_0$	$3{\cdot}8_5 \pm 0{\cdot}1_5$	$4{\cdot}5_5$†	$4{\cdot}1_5$	$0{\cdot}7_0 \pm 0{\cdot}1_5$	$0{\cdot}3_0 \pm 0{\cdot}1_5$	⊥
Diethyleneglycoldiacetate	$13{\cdot}1_5 \pm 0{\cdot}1_0$	$16{\cdot}5_5 \pm 0{\cdot}0_5$	$3{\cdot}6_5 \pm 0{\cdot}1_0$	$4{\cdot}5_5$	$4{\cdot}1_5$	$0{\cdot}9_0 \pm 0{\cdot}1_0$	$0{\cdot}5_0 \pm 0{\cdot}1_0$	∥?
Hexanediol-1:6	$13{\cdot}5_5 \pm 0{\cdot}1_5$	$17{\cdot}4_5 \pm 0{\cdot}1_0$	$4{\cdot}0_5 \pm 0{\cdot}1_5$	$4{\cdot}5_5$	$4{\cdot}1_5$	$0{\cdot}5_0 \pm 0{\cdot}1_5$	$0{\cdot}1_0 \pm 0{\cdot}1_5$	⊥
Pentanediol-1:5	$13{\cdot}6_5 \pm 0{\cdot}1_5$	$17{\cdot}4_5 \pm 0{\cdot}1_0$	$4{\cdot}1_5 \pm 0{\cdot}1_5$	$4{\cdot}5_5$	$4{\cdot}1_5$	$0{\cdot}4_0 \pm 0{\cdot}1_5$	0	⊥
2:4-Hexadiynediol-1:6	$13{\cdot}0_5 \pm 0{\cdot}0_5$	$16{\cdot}1_0$	$3{\cdot}5_5 \pm 0{\cdot}0_5$	—	$4{\cdot}1_5$	—	$0{\cdot}6_0 \pm 0{\cdot}0_5$	∥

* Molecular thicknesses calculated on the basis of v. d. Waal's radii given by Pauling.
† If the carboxyl group is oriented parallel to the clay surface.
∥ plane of aliphatic chain parallel to clay surface.
⊥ plane of aliphatic chain perpendicular to clay surface.

carbon chain perpendicular to the clay surface. To obtain agreement between the observed spacings and those calculated* for this molecular orientation requires a shortening of the contact distances by amounts up to 0·8 Å for two contacts, and these values lie within the limits given by GREENE-KELLY.

However, for the ketones and acetoaceticethylester, an orientation coplanar to the montmorillonite surface is more probable in order to place the negative carbonyl oxygen at an equal distance from both negative silicate surfaces. This orientation results in lower calculated spacings with required shortening of contact distances of only 0·5–0·6 Å as compared with 1·7–2·3 Å for the perpendicular orientation. The existence of the coplanar arrangement is supported by their spacings being smaller than the lowest spacings (13·3 Å) for perpendicular orientation quoted by GREENE-KELLY. Furthermore, if the postulated coplanar arrangements are correct, 2:4-hexadiynediol-1:6, which is a strictly linear molecule, should give rise to the same layer spacing. A good agreement has been obtained between its spacing and those of the coplanar-oriented molecules.

As to the remaining two groups of compounds (ethernitriles and polyethyleneglycoldiacetates) their spacings are on the borderline between what would be expected from perpendicular and from coplanar orientation. The reasons given above for a coplanar orientation of the carbonyl group apply equally well to the orientation of the nitrile group. Coplanar orientation of the nitriles would require a shortening of contact distances of only 0·4–0·5 Å as compared with $\simeq 1$ Å for the perpendicular orientation.

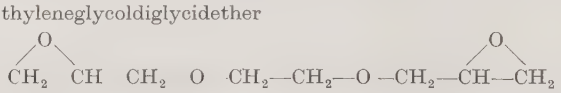
The polyethyleneglycoldiacetates should for the same reasons be oriented with their carboxyl groups coplanar to the clay surface. This does not necessarily result in a coplanar arrangement for the whole chain. However, it looks as if diethyleneglycoldiacetate with its shorter chain prefers an entirely coplanar orientation.

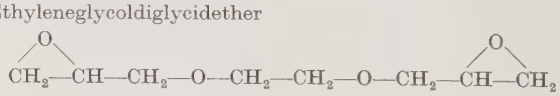
As data for the dimensions of the epoxide ring are not available, nothing can be said about the orientation of ethyleneglycoldiglycidether, but if the epoxide ring is hydrolysed on the clay surface, the spacing would indicate a perpendicular orientation.

The question of intermediate orientations also requires consideration. A small tilting of the perpendicular arrangement seems unlikely because it would tend to push the clay plates further apart due to the protruding hydrogens. A small tilting away from the parallel arrangement, where this is suggested, would place the dipoles in an unfavourable orientation and therefore seems unlikely.

The orientation of two-layer complexes is too uncertain to be discussed, because organic–organic distances and the degree of keying of the molecules are not known.

* The calculations have been made on the basis of the van der Waals radii of PAULING (1940) and the interatomic distances and bond angles given by the Chemical Society (1958) with the help of Stuart Briegleb molecular models to ascertain the features which determine the effective molecular thickness. The models themselves are based on slightly different radii than PAULING's, but we have felt it desirable to continue to use PAULING's values to facilitate comparison with other published data. In any case, conclusions drawn in the present work are not dependent on the particular set of radii employed.

I	1:3-Diketones	I_5	Acetylacetone $CH_3—CO—CH_2—CO—CH_3$
		I_7	α-Methoxyacetylacetone $CH_3—O—CH_2—CO—CH_2—CO—CH_3$
	+β-Ketoester	I_7'	Acetoaceticethylester $CH_3—CO—CH_2—COO—CH_2—CH_3$
II	1:4-Diketones	II_9	Nonanetrione-2:5:8 $CH_3—CO—CH_2—CH_2—CO—CH_2—CH_2—CO—CH_3$
		II_6	Hexanedione-2:5 $CH_3—CO—CH_2—CH_2—CO—CH_3$
III	Ether-nitriles	III_7	β:β′-Oxydipropionitrile $NC—CH_2—CH_2—O—CH_2—CH_2—CN$
		III_6	β-Ethoxypropionitrile $CH_3—CH_2—O—CH_2—CH_2—CN$
IV	Ether	IV_{11}	Bis-(2-ethoxyethyl)-ether $CH_3—CH_2—O—CH_2—CH_2—O—CH_2—CH_2—O—CH_2—CH_3$
		IV_9	Bis-(2-methoxyethyl)-ether $CH_3—O—CH_2—CH_2—O—CH_2—CH_2—O—CH_3$
	+ Glycidether	IV_{10}	Ethyleneglycoldiglycidether 
V	Ether-alcohols	V_8	Triethyleneglycol $HOCH_2—CH_2—O—CH_2—CH_2—O—CH_2—CH_2OH$
		V_5	Diethyleneglycol $HOCH_2—CH_2—O—CH_2—CH_2OH$
VI	Ether-esters	VI_{14}	Triethyleneglycoldiacetate $CH_3—COO—CH_2—CH_2—O—CH_2—CH_2—O—CH_2—CH_2—OCO—CH_3$
		VI_{11}	Diethyleneglycoldiacetate $CH_3—COO—CH_2—CH_2—O—CH_2—CH_2—OCO—CH_3$
VII	Alcohols	VII_6	Hexanediol-1:6 $HOCH_2—CH_2—CH_2—CH_2—CH_2—CH_2OH$
		VII_5	Pentanediol-1:5 $HOCH_2—CH_2—CH_2—CH_2—CH_2OH$
		VII_6'	2:4-Hexadiynediol-1, 6 $HOCH_2—C\equiv C—C\equiv C—CH_2OH$

II	1:4-Diketones	II_9	Nonanetrione-2:5:8 $CH_3—CO—CH_2—CH_2—CO—CH_2—CH_2—CO—CH_3$
		II_6	Hexanedione-2:5 $CH_3—CO—CH_2—CH_2—CO—CH_3$
IV	Ether	IV_{11}	Bis-(2-ethoxyethyl)-ether $CH_3—CH_2—O—CH_2—CH_2—O—CH_2—CH_2—O—CH_2—CH_3$
		IV_9	Bis-(2-methoxyethyl)-ether $CH_3—O—CH_2—CH_2—O—CH_2—CH_2—O—CH_3$
	+ Glycidether	IV_{10}	Ethyleneglycoldiglycidether 
V	Ether-alcohols	V_8	Triethyleneglycol $HOCH_2—CH_2—O—CH_2—CH_2—O—CH_2—CH_2OH$
		V_5	Diethyleneglycol $HOCH_2—CH_2—O—CH_2—CH_2OH$
VII	Alcohols	VII_6	Hexanediol-1:6 $HOCH_2—CH_2—CH_2—CH_2—CH_2—CH_2OH$
		VII_5	Pentanediol-1:5 $HOCH_2—CH_2—CH_2—CH_2—CH_2OH$

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References

Alder K. and Schmidt C. H. (1943), "Über die Kondensation des Furans und seiner Homologen mit a, β-ungesättigten Ketonen und Aldehyden. Aufbau von Di–, Tri–, Tetraketonen der Fettreihe". *Ber. Deut. Chem. Ges.* **76B,** 183–205. (see p. 196)

Barshad I. (1952), "Factors Affecting the Interlayer Expansion of Vermiculite and Montmorillonite with Organic Substances". *Soil. Sci. Soc. Am. Proc.* **16,** 176–82.

Bradley W. F. (1945), "Molecular Associations between Montmorillonite and Some Polyfunctional Organic Liquids". *J. Amer. Chem. Soc.* **67,** 975–81.

Brindley G. W. and Rustom M. (1958), "Adsorption and Retention of an Organic Material by Montmorillonite in the presence of Water". *Am. Mineralogist* **43,** 627–40.

Chemical Society, London (1958), Tables of Interatomic Distances and Configuration in Molecules and Ions. Special Publication No. 11.

Cowan C. T. and White D. (1958), "The Mechanism of Exchange Reactions Occurring between Sodium Montmorillonite and Various n-Primary Aliphatic Amine Salts". *Trans. Farad. Soc.* **54,** 691–7.

Greene–Kelly R. (1956), "The Sorption of Saturated Organic Compounds by Montmorillonite". *Trans. Farad. Soc.* **52,** 1281–6.

Greenland D. J. (1956), "The Adsorption of Sugars by Montmorillonite. II. Chemical Studies". *J. Soil Science* **7,** 329–34.

Grim R. E., Allaway W. H. and Cuthbert F. L. (1947), "Reaction of Different Clay Minerals with some Organic Cations". *J. Amer. Ceram. Soc.* **30,** 137–42.

Grim R. E. (1953), Clay Mineralogy, New York, Toronto, London. p. 261

Haxaire A. and Bloch J. M. (1956) "Sorption de molécules organiques azotées par la montmorillonite. Étude du méchanisme. *Bull. Soc. Franç. Min. Crist.* **79,** 464–75.

Hoffmann R. W. "Dichromate Oxidation Applied to the Concentration Determination of Aliphatic Compounds in Aqueous Solutions", submitted to 'the Analyst'.

Jordan J. W. (1949), "Alteration of the Properties of Bentonite by Reactions with Amines". *Mineralog. Mag.* **28,** 598–605.

MacEwan D. M. C. (1948), "Complexes of Clays with Organic Compounds. I. Complex Formation between Montmorillonite and Halloysite and certain Organic Liquids". *Trans. Farad. Soc.* **44,** 349–67.

MacEwan D. M. C. and Talibudeen O. (1949), "L'adsorption interlamellaire". *Bull. Soc. Chim. Franc.* 1949, E37–42.

Pauling L. C. (1940), The Nature of the Chemical Bond. Cornell University Press, Ithaca, N.Y.

Reppe W. und Mitarbeiter (1955), "Äthinylierung IV". *Ann. Deut. Chem. Liebigs.* **596,** 38–79. (see p. 70)

Ross W. C. J. (1950), "The Reaction of Certain Epoxides in Aqueous Solutions", *J. Chem. Soc.* 1950, 2257–72, (see p. 2271).

Skrabal A. and Zahorka A. (1925), "Über die Hydrolyse des Acetessigesters durch Säuren". *Monatsh. d. Chemie.* **46,** 559–74, (see p. 561).

Smith C. R. (1934), "Base Exchange Reactions of Bentonite and Salts of Organic Bases". *J. Amer. Chem. Soc.* **56,** 1561–3.

Talibudeen O. (1955), "Complex Formation between Montmorillonoid Clays and Amino Acids and Proteins". *Trans. Farad. Soc.* **51,** 582–90.

Torozzolo A. M. and Lieber E. (1950), "The Hydroxylamine Number; Application to the Identification of Ketones". *Anal. Chem.* **22,** 764–8.

Geochimica et Cosmochimica Acta, 1960, Vol. 20, pp. 30 to 44. Pergamon Press Ltd. Printed in Northern Ireland

Potentiometric titration and equivalent weight of humic acid*

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Abstract—The "acid nature" of humic acid has been controversial for many years. Some investigators claim that humic acid is a true weak acid, while others feel that its behaviour during potentiometric titration can be accounted for by colloidal adsorption of hydrogen ions. The acid character of humic acid has been reinvestigated using newly-derived relationships for the titration of weak acids with strong base. Re-interpreting the potentiometric titration data published by Thiele and Kettner in 1953, it was found that Merck humic acid behaves as a weak polyelectrolytic acid having an equivalent weight of 150, a pK_a of 6·8 to 7·0, and a titration exponent of about 4·8. Interdretation of similar data pertaining to the titration of phenol–formaldehyde and pyrogallol–formaldehyde resins, considered to be analogs for humic acid by Thiele and Kettner, leads to the conclusion that it is not possible to differentiate between adsorption and acid–base reaction for these substances.

Introduction

Soil organic matter has been classified on the basis of its solubility in various solvents such as acid, alkali or alcohol. In the following discussion humic acid is defined as the portion of soil organic matter that is soluble in alkali and insoluble in acid (Fraser, 1955).

For many years the "acid nature" of humic acid has been the subject of controversy; it has been disputed as to whether the material is titratable as an electrolyte, or whether it adsorbs hydrogen ions colloidally. Oden (1919) presented evidence that the material behaves as a true acid, whereas Thiele and Kettner (1953) reported that potentiometric titration of humic acid leads to erratic results. These latter workers, resorting to discontinuous titration to assure equilibrium conditions, concluded that humic acid, and other polymers they studied as humic acid analogs, cannot be titrated electrometrically, that the titrations show no end-point but resemble adsorption isotherms and, therefore, that humic acid does not behave as a true acid. For this reason, they concluded it to be impossible to determine the equivalent weight of humic acid by potentiometric titration. Mukherjee and Lahiri (1958) pointed out that the alkali salts of humic acid exhibit many properties of polyelectrolytes, but these investigators did not discuss potentiometric measurements.

Breger (1951) presented evidence based on infra-red spectra that the skeletal structures of humic acid and lignin are related and similar. His mechanism for the theoretical splitting of the lignin molecule, based on the Russell formula for lignin, is shown in Fig. 1. On the basis of this illustration he has pointed out: "Only one transformation in a single building block of the lignin molecule need occur to produce acidic properties. Multiple conversions along the molecular chain coupled, perhaps, with occasional chain cleavage through the formation of carboxyl groups . . . may lead to . . . humic acid . . ." Humic acid is then a complex polymer containing acidic phenolic and carboxyl groups.

* Publication authorized by the Director, U.S. Geological Survey.

The Russell formula for lignin (RUSSELL, 1948) shown in Fig. 1 serves not as an actual representation of lignin structure but merely as a guide for illustration of potential degradation reactions. The polyhydroxy chalcone similarly serves to illustrate the types of structures that are known to be present in humic acid.

From these theoretical considerations it was believed that humic acid should behave as a true electrolyte during potentiometric titration. It was, therefore, the immediate object of this current work to re-evaluate previously published conclusions regarding the acid nature of humic acid. To this end the data of

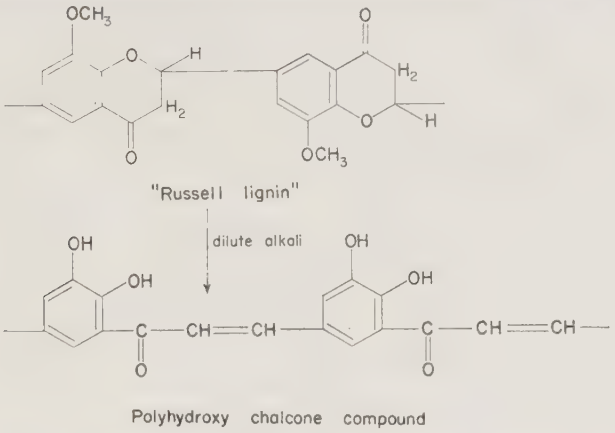

Fig. 1. Theoretical splitting of the lignin molecule (BREGER, 1959).

THIELE and KETTNER (1953), who used discontinuous titration to assure equilibrium conditions, have been reconsidered and re-interpreted. The ultimate objective of this study was to determine, if possible, the equivalent weight of humic acid for use in quantitative investigations of its chelating properties with a number of elements of geochemical interest.

In addition to study of humic acid, the excellent data for discontinuous titration of phenol–formaldehyde and pyrogallol–formaldehyde resins also published by THIELE and KETTNER, have also been reconsidered. THIELE and KETTNER, whose data are reproduced in Fig. 2, studied these resins as analogs of humic acid and concluded that they, as in the case of humic acid, also show no end-point upon titration and, therefore, that no equivalent weight can be determined for them.

Inasmuch as mere visual comparison of the curves of Fig. 2 was not sufficient for determination of the mechanism governing the change in hydrogen-ion concentration upon addition of alkali, the curves have been interpreted by graphical and mathematical methods devised for the purpose. It should be noted, however, that the titration curves for Merck humic acid, "humic acid" from glucose, and the ion-exchange resin do appear to have sigmoid shapes and inflexion points, whereas the curves for the two formaldehyde resins resemble adsorption isotherms.

In a discontinuous titration increasing multiples of an increment of titrant are added to a series of aliquots of a solution to be titrated; measurements, such as pH, can then be made in each reaction mixture and the values plotted against the

volume of titrant added. Equilibrium can be attained by permitting the reaction mixtures to stand for a sufficient length of time before the measurements are made. Also, it is then possible to repeat the measurements to confirm the attainment of equilibrium conditions. The curves of Fig. 3 were obtained by titrating 1 g quantities of each substance with varying volumes of 1 N NaOH while maintaining constant volume of the solutions at 100 ml. The millivolt readings shown were obtained by means of antimony–air and saturated calomel electrodes.

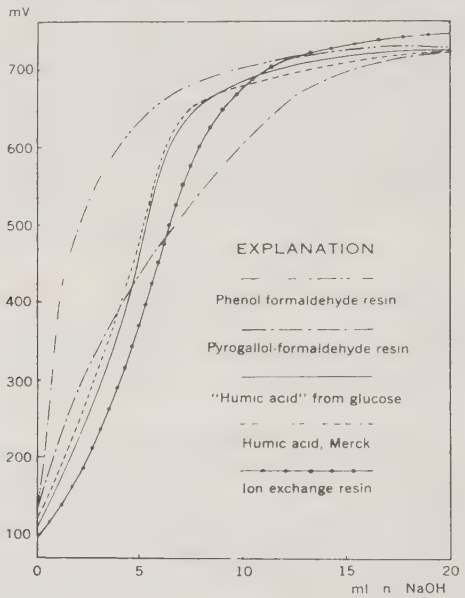

Fig. 2. Titration of humic acid and other compounds (Thiele and Kettner, 1953).

Millivolt readings were converted to pH units where necessary. To extract the published data with maximum accuracy, the curves shown in Fig. 2 were first enlarged photographically to 24 × 32 cm, and then scaled by means of a "GraphAnalogue" (Gerber, 1953). Co-ordinates could then be taken for desired points which were replotted or used in numerical calculations.

As the experimental points on Thiele and Kettner's curves could be identified from information given in their paper, it was possible to use the GraphAnalogue at these points. At the outset, it was felt best to utilize the data for Merck humic acid, a substance studied by many investigators, in the development of the theoretical aspects of the problem. Original data on a humic acid from another source will be published separately (Pommer and Breger, 1960).

Evaluation of Titration Curves as Adsorption Isotherms

Thiele and Kettner, as noted, called attention to the similarity of their curves to adsorption isotherms. Their data have, therefore, been evaluated for conformance with the Freundlich adsorption isotherm (Glasstone, 1946,

p. 555) which can be represented by the equation

$$a = kc^n$$

where a is the amount of solute adsorbed per unit weight of adsorbent from a solution of equilibrium concentration c, and k and n are constants and a plot of log a vs. log c yields a straight line.

Therefore, if the data reported by Thiele and Kettner truly show the titration of humic acid to represent adsorption of hydrogen ions, proper substitution of their data in the above logarithmic equation would be expected to yield a straight line plot and prove their conclusion.

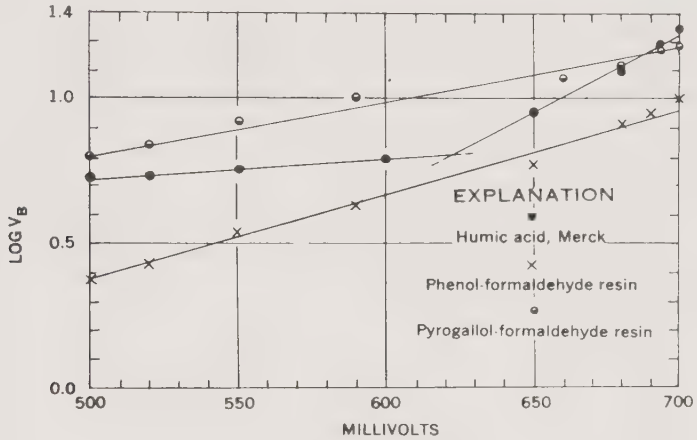

Fig. 3. Plot of log V against millivolts for discontinuous titrations of Merck humic acid, phenol–formaldehyde resin and pyrogallol–formaldehyde resin. Titration data from Thiele and Kettner (1953).

The solute removed from solution during titration is the hydrogen ion. As a pH value is the negative logarithm of the hydrogen ion concentration, it is possible to substitute millivolt readings for log a directly in the isotherm. The amount of hydrogen ion absorbed decreases with the amount of NaOH added, and the logarithm of this volume can be used for log c in the isotherm. Therefore, if titration involves a true adsorption of hydrogen ions, a plot of millivolts against the logarithm of millilitres NaOH added should yield a straight line. Fig. 3 shows such plots based on Thiele and Kettner's data for the titration of Merck humic acid, phenol–formaldehyde resin, and pyrogallol-formaldehyde resin. Plotted this way, data for the two resins yield straight lines; the data for humic acid, on the other hand, form two intersecting straight lines.

Gran (1952) has shown that, if a polymeric acid is titrated with a strong base, a plot of V against $V \cdot 10^{(K-\mathrm{pH})/n}$ will result in a straight line in the region before the end point is reached where V is the amount of base added and K and n are constants. From this relation it can be seen that a plot of pH vs. log V in the region before the end-point has been reached will also result in a straight line for all practical purposes. Similarly, in the region after the end-point has been reached, a plot of V against $(V_0 + V)10^{\mathrm{pH}-\mathrm{K}}$ will result in a straight line where V_0

is the volume of the acid before titration. In the case of a discontinuous titration where the volume of the solution is held constant, $(V_0 + V)$ is equal to V and, therefore, a plot of pH or millivolts against log V will result in a straight line but with a different slope. Hence, two straight lines which intersect are to be expected if pH or millivolts are plotted against the logarithm of titrant volume added when a polymeric acid is titrated with a strong base. The point of intersection represents the end-point.

It is clearly evident from the above considerations that the data for Merck humic acid as plotted in Fig. 3 do not lead to the straight-line relationship to be expected were an adsorption isotherm involved. Rather, the calculations based on Gran's equations lead to results completely consistent with those to be expected when a weak polymeric acid is titrated with a strong base. In view of this conclusion it is possible to calculate the equivalent weight of humic acid from Fig. 3.

The intersection of the two straight lines for humic acid occurs at 622 mV. This value corresponds in Fig. 2 to the addition of 6·7 ml of 1 N NaOH for the neutralization of 1 g of humic acid. One gramme of humic acid, therefore, contains 6·7 mEq and its equivalent weight is 150.

Although the application of Gran's equations to semilogarithmic plotting of titration curves involves a simplification, the transformed functions do not deviate significantly from linearity within a reasonable distance from the point of intersection.

In view of the possibility that a deviation from linearity might have affected the point of intersection of the two straight lines in Fig. 3 and hence the equivalent weight of the humic acid, the determination of this value was repeated using the original method of Gran (1952) in which V is plotted against $10^{k-\mathrm{pH}}$. In this connexion it must be pointed out that this method cannot be used conveniently if the end-point is not known approximately. If a titration curve extending over 10 pH units is plotted in its entirety the antilogarithmic pH values will range from 1 to 10^{10} and will be impossible to plot except in several regions using several k-values, where k according to Gran, is an arbitrary constant. If a tentative value for V_e is established, however, it is easy to assume a k of such value that, whenever V is plotted against $V \cdot 10^{k\ \mathrm{pH}}$, the point of intersection between the two lines falls on the portion plotted, even if an antilogarithmic value of 100 is not exceeded. A redetermination of the equivalent weight of humic acid by this method yielded a value of 151, which was practically identical with the original value of 150. This result illustrated that the end-point obtained by plotting log V against pH (Fig. 3) was correct.

Confirmation of Electrolytic Character of Humic Acid

The evidence supports the conclusion that titration of humic acid with strong base does not follow an adsorption isotherm. The data, moreover, are not inconsistent with those anticipated for the titration of a weak electrolyte, an observation not unexpected in view of theoretical considerations regarding the chemical structure of humic acid.

To verify the electrolytic nature of humic acid, a relationship has been derived between pH and V_B, the volume of base added when a weak polyelectrolytic acid

is titrated with a strong base. This relationship has made it possible to plot pH vs. a function of V_B as a straight line. Comparison of THIELE and KETTNER's experimental data with the theoretical relationship was then carried out to determine the degree of fit.

Conversion of millivolt readings to pH *units*

THIELE and KETTNER reported their titrations in terms of millivolts, potential differences between saturated calomel and antimony–air electrodes. PERLEY (1939) pointed out that the millivolt reading of an antimony electrode in a solution under an atmosphere of nitrogen is 30 per cent higher than in the same solution under oxygen if the pH of the solution is 3·95; under the same circumstances, the reading is 10 per cent higher if the pH is 11·04 at 25°C. The change in millivolts per pH unit of an acid solution under nitrogen is 52, and that of an alkaline solution is 58; under an oxygen atmosphere the values are 59 for an acid solution and 50 for an alkaline solution. Air gives an intermediate value in all cases. Humic acids have been reported to be quite resistant to oxidation (KUKHARENKO, 1950). It is, therefore, doubtful that millivolt readings with an antimony electrode will vary from those taken in air as a result of any differential uptake of oxygen by humic acids with consequent enrichment of nitrogen.

Although no complication arises from the atmosphere under which titration with an antimony electrode is carried out, BRITTON (1955, p. 100) has pointed out that hydroxy acids do affect the electrode. Inasmuch as humic acids have constituent hydroxyl groups, some irregularities in the titration curve may be expected.

Estimation of pH values was made on the basis of the following considerations. PERLEY's data (1939) indicate that a ratio of 57 mV per pH unit is reasonable for an antimony–air electrode at ambient temperature. THIELE and KETTNER's millivolt readings were, therefore, divided by 57 to yield uncorrected pH values. Further correction for liquid junction potentials and other factors affecting the true reading was made as follows: if 10 ml of 1 N NaOH are added to a solution made up to a final volume of 100 ml, the solution contains 10 m-moles of NaOH per 100 ml of solution, or 0·1 mole/l. If 1 g of humic acid has previously been added to the solution, that solution is 0·1 N except for the amount of NaOH neutralized by the humic acid. If the equivalent weight of the humic acid exceeds 100, there is less than 0·1 mole of humic acid in solution and, therefore, an excess of sodium ions.

Under these conditions the solution contains sodium hydroxide and sodium humate, but no free humic acid. As was noted, the equivalent weight of the humic acid is 150, and 1 g of humic acid contains 6·7 mEq of the material. The solution to which 10 ml of 0·1 N NaOH was added contains, therefore, 33 mEq of NaOH per l., and the pH of this solution should be

$$-\log K_{H_2O} + \log [OH] = pH$$
$$14 + \log [0{\cdot}033] = 12{\cdot}52$$

Referring to Fig. 2, a solution containing 1 g of Merck humic acid and 10 ml of 1 N NaOH gives a reading of 681 mV corresponding to an uncorrected pH value of

681/57 or 11·85. Inasmuch as this solution should have a pH value of 12·52 as shown above, the correction factor of (12·52 — 11·85) or 0·67 pH units was added to obtain the calculated pH values shown in Tables 1 and 2.

Table 1. Data used in construction of Fig. 4
(based on data by Thiele and Kettner, 1953)

mV*	pH†	V_B‡	$\tanh^{-1}(0{\cdot}3V_B - 1)$
173	3·68	0·8	−1·00
182	3·84	1·0	−0·87
199	4·13	1·2	−0.76
214	4·39	1·4	−0·66
232	4·71	1·6	−0·58
244	4·92	1·8	−0·50
258	5·16	2·0	−0·42
265	5·28	2·2	−0·35
282	5·58	2·4	−0·29
291	5·73	2·6	−0·22
310	6·06	2·8	−0·16
322	6·27	3·0	−0·10
335	6·50	3·2	−0·04
353	6·81	3·4	0·02
369	7·09	3·6	0·08
389	7·44	3·8	0·14
406	7·73	4·0	0·20
422	8·01	4·2	0·27
439	8·31	4·4	0·33
456	8·60	4·6	0·40
484	9·09	4·8	0·47
494	9·27	5·0	0·55
517	9·67	5·2	0·63
534	9·96	5·4	0·72
555	10·33	5·6	0·83
574	10·66	5·8	0·95
583	10·81	6·0	1·10

* Millivolt reading of antimony-air electrode/calomel electrode couple (see Fig. 2).
† Calculated from millivolts by method described in text.
‡ Millilitres of 1 N NaOH added (see Fig. 2).

Linearization of titration curve for a weak polymeric acid before neutralization

Kilpi (1938) pointed out that most weak polymeric acids can be treated as monobasic acids. Such an acid can be represented by $(HA)_x$ where x is the number of monomers in the molecule and A is the monomeric acid group from which one hydrogen ion may dissociate:

$$HA \rightleftharpoons H^+ + A^-$$

Superscripts indicating charges will be omitted for simplicity.

The structure A may be relatively simple and may represent a repetitive chemical monomer, or it may represent a complex of various structures such as occur in certain natural polymers. In the latter case the equivalent weight of A will be of the number-average type (Bonnar *et al.*, 1958, p. 2).

Table 2. Data used in construction of Fig. 5
(based on THIELE and KETTNER, 1953)

mV*	pH†	V_B‡	log (V_B − 6·7)
634	11·70	7·0	−0·52
664	12·22	8·0	0·11
671	12·35	9·0	0·36
681	12·52	10·0	0·52
688	12·64	11·0	0·63
691	12·69	12·0	0·72
695	12·76	13·0	0·80
701	12·87	14·0	0·86
703	12·90	15·0	0·92

* Millivolt reading of antimony–air electrode/calomel electrode couple (Fig. 2).
† Calculated from mV by method described in text.
‡ Millilitres of 1 NaOH added (Fig. 2); 0·2 ml intervals were interpolated until V_B reached the value of 8·0. In the region beyond this value, 1 ml intervals were taken owing to the flatness of the curve; beyond 15·0 ml the curve was too flat to be studied further.

If HA is titrated with strong base, the amount of acid neutralized or ionized, A, is equivalent to the base added, B. Ignoring for the time being that HA may be a repeating monomeric unit of a polymer, and requiring only that it be a weak acid, its ionization constant K_a is

$$K_a = \frac{H \cdot A}{HA}$$

where H, A, and HA represent the activities of the respective species. In the following discussion activitity coefficients will be considered to be unity.

If $pK_a = -\log K_a$, and α is the degree of neutralization, the Henderson–Hasselbalch equation can be written as

$$pH = pK_a - \log \frac{1 - \alpha}{\alpha} \qquad (1)$$

In the case of a polymeric acid, this equation must be generalized (KATCHALSKY and SPITNIK, 1947) to

$$pH = pK_a - n \log \frac{1 - \alpha}{\alpha} \qquad (2)$$

where n is termed the titration exponent; this factor is introduced to correct for changes in the ionization constant (pK_a) as the change from an uncharged to a partly charged cationic bond alters the electrostatic field of the humic acid molecule during the course of a titration.

Because values of α must lie between zero and one, the use of equation (2), which applies to the titration of a weak acid with a strong base, is invalid after complete neutralization.

If the weak acid is 50 per cent neutralized, then

$$\alpha = 1 - \alpha = 0{\cdot}5$$

and $pH = pK_a$. Using the subscript $\frac{1}{2}$ to denote this point, it is found from equations (1) and (2) that

$$pH_{1/2} = pK_a - n \log \frac{HA_{1/2}}{A_{1/2}} = pK_a + n \log \frac{A_{1/2}}{HA_{1/2}}$$

and it follows from equation (1) and the definition of A_t that

$$HA_{1/2} = A_{1/2} = \frac{A_t}{2}$$

If a solution of a weak polymeric acid at $pH_{1/2}$ is titrated with a strong base B, each addition of B will result in the formation of an equivalent amount of A. The ionized acid at any point is then

$$A_{1/2} + B = \frac{A_t}{2} + B$$

The remaining unionized acid is

$$\left(\frac{A_t}{2} - B\right)$$

and equation (2) becomes

$$pH = pK_a + n \log \frac{(A_t/2) + B}{(A_t/2) - B}$$

or

$$pH = pK_a + n \log \frac{(1 + 2B/A_t)}{(1 - 2B/A_t)} \tag{3}$$

where B is the amount of base added after $pH_{1/2}$ has been reached. Equation (3) is also valid if $pH < pH_{1/2}$, in which case B represents the amount of base to be added to reach $pH_{1/2}$ and is a negative number. At $pH_{1/2}$, B is zero. As α varies between zero and one, it then follows that

$$-\frac{A_t}{2} < B < \frac{A_t}{2}$$

Under these conditions, $B = -A_t/2$ before any base has been added, and $B = A_t/2$ at the equivalence point.

Using the inverse hyperbolic function

$$\tanh^{-1} x = \frac{2{\cdot}303}{2} \log \frac{1 + x}{1 - x}$$

or

$$\log \frac{1 + x}{1 - x} = 0{\cdot}8686 \tanh^{-1} x \tag{4}$$

and substituting in equation (3), the following relationship is obtained:

$$pH = pK_a + 0{\cdot}8686\, n \tanh^{-1} \frac{2B}{A_t} \tag{5}$$

where B is the amount of base added after $pH_{1/2}$ has been reached. If B_t is defined as the total amount of base added, then

$$B_t = B + B_{1/2}$$

where $B_{1/2}$ is the amount of base added to reach $pH_{1/2}$. This amount of base is equal to $A_t/2$,

hence $$B_t = B + \frac{A_t}{2}$$

and $$B = B_t - \frac{A_t}{2}$$

Substituting in equation (5),

$$pH = pK_a + 0{\cdot}8686\, n \tanh^{-1}\left(\frac{2B_t}{A_t} - 1\right) \qquad (6)$$

It must be remembered that B_t is the total amount of base added. Starting with a solution of an acid containing salt of the acid, B_t includes the amount of base necessary to form that amount of salt present. In the case of a discontinuous titration it makes no difference in what order the solutions were prepared, and back-titration of a salt with acid can be treated exactly the same as forward titration. There is no dilution effect if all solutions are made up to constant volume; if changes in volume are relatively small they can be disregarded. As Thiele and Kettner and others have noted, salts of other acids may have a slight effect on the titration. The amount of base added in milliequivalents, B_t, can be given as

$$B_t = NV_B$$

where N is the normality of the solution and V_B the volume in millilitres of solution added and

$$pH = pK_a + 0{\cdot}8686\, n \tanh^{-1}\left(\frac{2NV_B}{A_t} - 1\right) \qquad (7)$$

If titration of a humic acid solution with alkali is a true potentiometric titration, the portion of the titration curve before equivalence is reached should conform to equation (7). A convenient way to test this conformance is by transforming equation (7) to a linear form. Equation (7) has the form

$$y = a + b \tanh^{-1} x$$

which can be transformed to a linear form by plotting y against $\tanh^{-1} x$. Therefore, a plot of pH vs.

$$\tanh^{-1}\left(\frac{2NV_B}{A_t} - 1\right)$$

should give a straight line. If Thiele and Kettner's data yield a straight line when plotted in this way, humic acid must be a weak polyelectrolytic acid.

Application of linear relation to titration data

The titration of humic acid with NaOH by Thiele and Kettner is based on twenty-one points and represents twenty-one reaction mixtures differing from

each other by 1 ml increments of alkali. As the equivalence point was reached prior to the addition of 7 ml of NaOH, the seven points based on exact experimental data were not sufficient for a satisfactory sampling of the curve. Because the curve was smooth and without irregularities, it was felt that a sampling of the curve at intervals representing 0·2 ml additions would be preferable, and the interpolations were made with the GraphAnalogue (Gerber, 1953). The three outermost points on both ends of the curve were disregarded because they approached the region where the function tended toward infinity. Computation of the pH values has been discussed; V_B was the number of millilitres of NaOH added as taken from the graph; the normality of the NaOH (N) was one; A_t, the amount of humic acid present, was previously determined to be 6·7 milliequivalents; and

$$\frac{2NV_B}{A_t} = 0{\cdot}3V_B$$

Using the data of Table 1 for twenty-seven points taken from Thiele and Kettner's curve, a plot of pH vs. $\tanh^{-1}(0{\cdot}3V_B - 1)$ was constructed (Fig. 4).

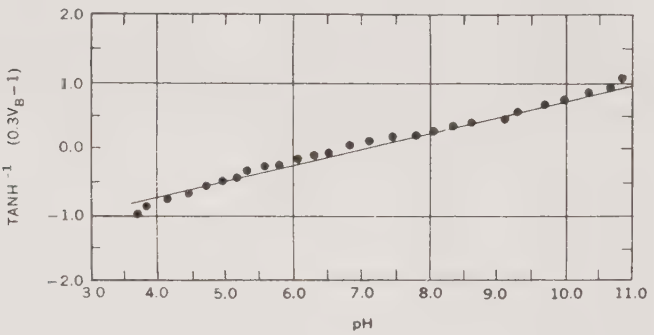

Fig. 4. Plot of $\tanh^{-1}(0{\cdot}3V - 1)$ against pH based on Thiele and Kettner's data.

The straight line connecting the points is based on a least squares calculation leading to the following relationship

$$\text{pH} = 7{\cdot}0 + 4{\cdot}2 \tanh^{-1}(0{\cdot}3V_B - 1)$$

Comparing this relation to equation (7), the pK_a for humic acid is 7·0 and its titration exponent is (4·2/0·87) or 4·8. This procedure has shown that humic acid behaves as a true acid on potentiometric titration in the region prior to neutralization.

Linearization of titration curve for a weak polymeric acid after neutralization

In the region beyond the equivalence point a different relationship holds. Gran (1952) pointed out that in this case the relations are similar for strong acids, weak acids and polymeric acids titrated by strong base, and gives

$$C_{OH} = \frac{C_B(V_B - V_e)}{(V_0 + V_B)}$$

where C_{OH} is the concentration of hydroxide ions, C_B the concentration of the added base, V_0 the original volume of the acid, V_B the volume of base added and V_e the volume of base necessary to reach the equivalence point. In a discontinuous titration there is no change in volume from point to point. Where there is no dilution factor,

$$C_{OH} = \frac{C_B(V_B - V_e)}{V_t}$$

where V_t is the total volume.
But

$$C_H = \frac{K_w}{C_{OH}}$$

where K_w is the ionization constant of water, and

$$C_H = \frac{K_w V_t}{C_B (V_B - V_e)}$$

$$\log C_H = \log K_w + \log V_t - \log C_B - \log (V_B - V_e)$$

and

$$pH = \log (V_B - V_e) + \log C_B - \log K_w - \log V_t;$$

C_B, the normality of the NaOH solution used in Thiele and Kettner's experiment, was 1; V_e (as mentioned previously) was 6·7 ml; K_w is 10^{-14}; and V_t was 100 ml; hence

$$pH = \log (V_B - 6{\cdot}7) + 0 - (-14) - 2 = \log (V_B - 6{\cdot}7) + 12$$

and a plot of pH against log $(V_B - 6{\cdot}7)$ in the region after equivalence had been reached should yield a straight line with a slope of 1 and an intercept of 12. Such a plot was constructed on eight points of Thiele and Kettner's curve using 1 ml intervals. The portion of the curve beyond a value for V_B of 15 ml was not used owing to its flatness. Table 2 shows the data used in construction of this curve (Fig. 5) which yielded a least squares line

$$pH = 0{\cdot}83 \log (V_B - 6{\cdot}7) + 12{\cdot}11$$

which fits the expected line reasonably well. This procedure has shown that humic acid behaves as a true acid on potentiometric titration in the region after neutralization.

Evaluation of Calculations Regarding Merck Humic Acid

The volume of 1 N NaOH required to neutralize 1 g of Merck humic acid in Thiele and Kettner's titration was 6·7 ml (see Fig. 3). This value can be confirmed by a consideration of the equation relating pH as a function of $\tanh^{-1}$ $(0{\cdot}3 V_B - 1)$. Here the factor of 0·3 is dependent upon use of a correct value for V_e (6·7); choice of an incorrect value causes deviation of the derived plot from linearity.

An equivalent weight of 150 has been calculated for Merck humic acid; this value compares closely to 147 found by Stadnikoff and Korschew (1929), and to 152 reported by Scheele *et al.* (1935).

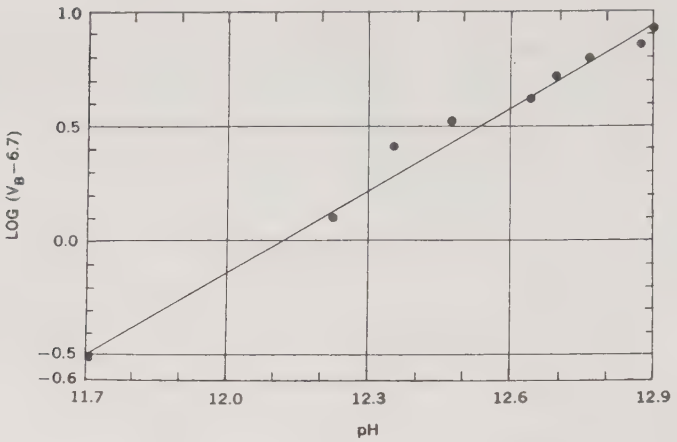

Fig. 5 Plot of log (V_B — 6·7) against pH based on Thiele and Kettner's data.

The pK_a for humic acid was found to be 7·0 from the relationship between pH and $\tanh^{-1}$ (0·3V_B — 1). An alternative computation of this value can be made by use of the Katchalsky–Spitnik equation (equation 2) when the degree of neutralization is set equal to 0·5. At this point pH = pK_a, and $V_B = 0{\cdot}5V_e$, or 3·4. This corresponds to a pH of 6·8 and the pK_a is 6·8. The values of pK_a computed by these alternative methods, 7·0 and 6·8, are quite similar.

The titration exponent of 4·8 is subject to error. The value was obtained by taking the slope of a rather steep line; slight errors in the slope will affect the value considerably.

The consistency of all the derived data reflect the excellence of Thiele and Kettner's original experimental work. The various lines of evidence, however, demonstrate with little doubt that titration of the humic acid represents neutralization of a weak polyelectrolytic acid and not colloidal adsorption of hydrogen ions.

Interpretation of Titration Data for Analogs of Humic Acid

Because the shapes of the titration curves for glucose "humic acid" and the ion exchange resin resembled the curve for Merck humic acid (Fig. 2), it appeared reasonable to assume that the behaviour of these substances was similar to that of the Merck humic acid. For this reason these curves were not further examined. In contrast to these S-shaped curves, the titration curves for the phenol–formaldehyde and pyrogallol-formaldehyde resins exhibited no inflexion points, resembled adsorption isotherms and, on logarithmic plotting (Fig. 3), yielded straight lines. To examine the possibility that these two titration curves might still represent neutralizations rather than adsorption phenomena, an attempt was made to distinguish between these two mechanisms. In the case of the Merck humic acid, derivation of the equations was based upon the existence of an equivalence point. As titration of the formaldehyde resins led to no inflexion point, and as those resins should be weak polyelectrolytic acids on the basis of chemical considerations, conditions leading to the appearance or disappearance of an end-point during titration were considered. It has already been pointed out that polyelectrolytic

acids behave as a monobasic acids. Ricci (1952) discussed the shape of titration curves of weak monobasic acids neutralized with strong base. Inspection of Fig. 2 indicates that the phenol–formaldehyde and pyrogallol–formaldehyde resin neutralization curves and Ricci's curve for a weak, dilute acid resemble each other. It does not appear possible to distinguish between the shape of these curves and an adsorption isotherm. Roller (1928) also pointed out that very weak dilute acids on titration will not show an end-point unless the product of the ionization constant of the acid and its concentration exceeded $27 \cdot 10^{-14}$. Therefore, it is not possible to determine whether titration of the phenol–formaldehyde and pyrogallol–formaldehyde resins can best be explained as an adsorption phenomenon or merely as neutralization of a very weak, very dilute electrolyte.

Summary and Conclusions

Discontinuous titration data reported by Thiele and Kettner (1953) for Merck humic acid and several compounds considered as analogs have been reinterpreted by graphical and mathematical techniques. The following conclusions are based in part on the derivation of new relationships governing the potentiometric titration of weak monobasic and polyelectrolytic acids with strong bases.

(1) Upon potentiometric titration with strong base, Merck humic acid behaves as a polyelectrolytic weak acid with an equivalent weight of 150 and a titration exponent of about 5. Values of pK_a calculated in two ways were 6·8 and 7·0. Contrary to Thiele and Kettner's conclusions, the data do not support the conclusion that humic acid adsorbs hydrogen ions colloidally during titration.

(2) The assumption appears reasonable that the "humic acid" from glucose and the ion exchange resin presented as analog compounds behave in a manner similar to that of Merck humic acid during potentiometric titration.

(3) It is not possible to determine whether the behaviour of the phenol–formaldehyde and pyrogallol–formaldehyde resins during titration represent colloidal adsorption of hydrogen ions, or whether it represents the titration of a weak dilute acid under conditions where the product of the concentration and the ionization constant of the acid is less than $27 \cdot 10^{-14}$.

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References

Bonnar R. U., Dimbat M. and Stross F. H. (1958) Number-Average Molecular Weights. Interscience, New York.

Breger I. A. (1951) Chemical and structural relationship of lignin to humic substances. *Fuel* **30,** 204–208.

Breger I. A. (1959) Origin of petroleum: Reaction of metabolically significant organic compounds in diagenetic environments. Preprints of the *Papers of the General Petroleum Geochemistry Symposium, Fordham University, New York* pp. 77–88.

Britton H. T. S. (1955) *Hydrogen Ions, their Determination and Importance in Pure and Industrial Chemistry* (4th Ed.) Vol., 1, p. 476. Chapman & Hall, London.

Fraser G. K. (1955) Soil organic matter. *Chemistry of the Soil*, (Edited by Bear F. E.) p. 163. Reinhold, New York.

Gerber H. J. (1953) *The Gerber GraphAnalogue—An instruction manual for Model GA-103.* Bull. No. 500. The Gerber Scientific Instrument Company, Hartford, Connecticut.

Glasstone S. (1946) *The Elements of Physical Chemistry.* D. Van Nostrand, New York.

Gran G. (1952) Determination of equivalence point in potentiometric titrations—II. *Analyst* 77, 661–671.

Katchalsky A. and Spitnik P. (1947) Potentiometric titration of polymethacrylic acid. *J. Polym. Sci.* **2,** 432–446.

Kilpi S. (1938) Einige Bemerkungen wegen der Abhandlung von Werner Kern; über heterogene Molekülkolloide—I. *Z. phys. Chem.* A **181,** 473–474.

Kukharenko T. A. (1950) Investigation in the field of humic acids. *Proceedings of the Institute of Fossil Fuels, U.S.S.R. Academy of Science* **2,** 208–226.

Mukherjee P. N. and Lahiri A. (1958) Polyelectrolytic behaviour of humic acids. *Fuel* **37,** 220–226.

Oden S. (1919) Die Huminsäuren. Chemische, physikalische und bodenkundliche Forschungen. *Kolloid Beih.* **11,** 75–260.

Perley G. A. (1939) Characteristics of the antimony electrode. *Industr. Engng. Chem. (Anal.)* **11,** 319–322.

Pommer A. M. and Breger I. A. (1960) Equivalent weight of humic acid from peat. *Geochim. et Cosmochim. Acta.* **20,** 45–50.

Ricci J. E. (1952) *Hydrogen Ion Concentration. New Concepts in a Systematic Treatment* Princeton University Press, Princeton.

Roller P. S. (1928) Theory of the end-point in electrometric titration. *J. Amer. Chem. Soc.* **50,** 1–8.

Russell A. (1948) Interpretation of lignin—I. The synthesis of gymnosperm lignin. *J. Amer. Chem. Soc.* **70,** 1060–1064.

Scheele W., Schulze W. and Spandau H. (1935) Über Huminsäuren. *Kolloid-Z.* **72,** 301–312.

Stadnikoff G. and Korschew P. (1929) Zur Kenntnis der Huminsäuren. *Kolloid-Z.* **47,** 136–141.

Thiele H. and Kettner H. (1953), Über Huminsäuren. *Kolloid-Z.* **130,** 131–160.

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Equivalent weight of humic acid from peat*

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Abstract—By means of discontinuous titration, the equivalent weight of humic acid isolated from a peat was found to increase from 144 to 183 between the third and fifty-second day after the humic acid was dissolved. Infra-red studies showed that the material had probably condensed with loss of carbonyl groups.

Introduction

Gruner (1922) showed that peat solutions are effective solvents for a number of iron minerals; other authors (Rankama and Sahama, 1950, p. 346; Bateman, 1951, p. 144) have suggested an important role for humic substances in the weathering and redistribution process for other minerals and elements. In an attempt to prepare humic acid solutions of known normality for quantitative geochemical studies, Pommer and Breger (1960) showed that it is possible to determine the equivalent weight of humic acid (Merck) by potentiometric titration. That study, theoretical in nature and based on the data published by Thiele and Kettner (1953), has been extended by the determination of the equivalent weight of a different humic acid isolate.

Preparation of Humic Acid

Humic acid was prepared from peat by a method patterned after that of Puri (1949, p. 222). The peat, obtained through the courtesy of Professor F. M. Swain, University of Minnesota, was from the Cedar Creek Forest Preserve, Anoka and Isanti Counties, Minnesota.

The peat sample (2000 g), which was very fibrous and contained small twigs and rootlets, was treated with 8 l. of 0·1 N HCl, heated until the solution started to boil, cooled, filtered and washed until the pH of the filtrate reached a value of from 3·6 to 3·9. The peat was then treated with 15 l. of a solution containing 16·0 g/l. of NaOH and 21·2 g/l. of Na_2CO_3 for 3 hr at 75°C, cooled, and filtered under suction through a glass fibre filter backed by a pad of Celite 545. The filtrate was refiltered and neutralized by dropwise addition of 1 l. of concentrated HCl while stirring vigorously. The brown precipitate of humic acid was separated by centrifugation and then purified by dialysis until no chloride ion could be detected in the dialysate. The humic acid was recovered and dried on the steam bath to give 81·5 g of a black, shiny, friable product (crude yield, 4·1 per cent).

The moisture content of the humic acid, as determined by its weight loss on heating to 105°C for about 2 hr, was 6·25 per cent. The dried humic acid contained 53·71 per cent carbon, 4·16 per cent hydrogen, and 6·06 per cent ash; on a moisture- and ash-free basis, 57·17 per cent carbon, and 4·43 per cent hydrogen

* Publication authorized by the Director, U.S. Geological Survey.

(analysis by Professor Mary Aldridge, The American University, Washington, D.C.). After correction for moisture and ash content, each gram of crude product contained 0·873 g humic acid.

A solution containing 1 g/l. of the crude humic acid was analysed oxidimetrically by the method of Kreulen (1932), and quadruplicate determinations showed the solution to contain 0·897 ± 0·024 g/l. of humic acid; this value differed from the calculated value by one standard error and served as a check on it.

Potentiometric Studies

The isolated humic acid (172 mg; 150 mg on a moisture- and ash-free basis) was dissolved in 20 ml N KOH (carbon-dioxide free) under nitrogen and allowed to stand for 1 week at room temperature to assure complete peptization. To this solution 18 ml 1N HCl were added, and the reaction mixture was diluted to 100 ml in a volumetric flask. The KCl formed in this reaction was intended to sharpen the end-point (Kilpi, 1943) and to minimize activity changes (Harned and Owen, 1958). Aliquots of 10 ml were taken; one aliquot constituted the "initial value", and multiples of 0·2 ml of 0·1 N HCl were added to the other aliquots by means of an automatic burette capable of delivering as little as 0·001 ml. The pH of each reaction mixture was determined with a pH-meter 30 min, 3 days, 9 days, and 52 days after mixing. Results are plotted in Fig. 1.

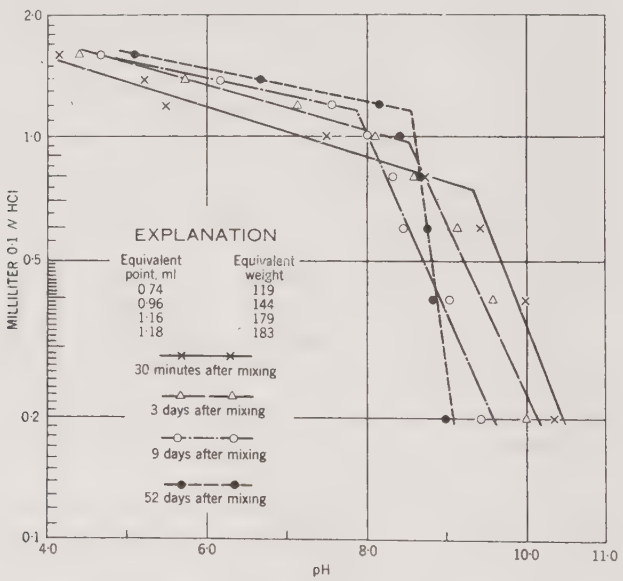


Fig. 1. Discontinuous potentiometric titration of humic acid.

Pommer and Breger (1960) showed that if a weak polymeric acid is titrated with a strong base, and the logarithm of V, the volume of base added (or acid if it is a back titration), is plotted against pH, two lines will be formed which, for all practical purposes, will be straight and which will intersect at the equivalence point. Plotting V against pH on the semilogarithmic scale of Fig. 1, it can be

seen that the volume of acid necessary to reach the equivalence point varies between 0·96 and 1·18 ml, except in the 30 min titration. In this case the value of 0·74 ml was obtained, possibly because insufficient time was allotted for the attainment of equilibrium.

If addition of 0·96 ml 0·1 N HCl to the reaction mixture results in equivalence, then the number of *equivalents* of NaOH required to neutralize the humic acid present (15·0 mg) is given by the expression (KOH present — HCl added originally — HCl added during titration), that is, 104 mEq. or 0·104 ml 1 N NaOH. The equivalent weight of the humic acid is then 15·0/0·104 or 144. Similarly, when addition of 1·18 ml 0·1 N HCl is required, the equivalent weight becomes 15·0/0·082 or 183. Hence, the equivalent weight of the humic acid increased from 144 to 183 between the third and fifty-second day after the solutions had been initially mixed. The equivalent weight of the humic acid 30 min after mixing was 119; in view of the findings by Thiele and Kettner (1953) that equivalent weights of humic acid measured shortly after mixing appear erratic and irreproducible, and in view of subsequent increases in the value noted in this work, the 30 min value must be considered to be unreliable.

Infra-red Studies

Inasmuch as the pH measurements indicated a change in composition of the solution with time, three of the reaction mixtures were selected for infra-red studies in an attempt to determine any changes in chemical structure of the humic acid that occurred on standing. The following solutions, which stood for 52 days, were chosen for this work: the most acid solution, with a final pH of 6·65; an "intermediate" solution, with a final pH of 8·0; and the most alkaline solution, with a final pH of 9·0. These solutions were each evaporated to dryness under nitrogen to obtain the residue. Powdered humic acid, as originally prepared, was examined for comparison. Potassium bromide discs containing a concentration of 1 per cent of each residue were prepared, and absorption curves of these discs (Fig. 2) were obtained using a Perkin–Elmer model 21 double-beam spectrophotometer with rock salt optics.

Fig. 2 shows that samples of humic acid recovered from the three solutions all have essentially the same infra-red absorption characteristics. Of particular interest is the fact that treatment of humic acid with acid or alkali has led to the loss of the strong carbonyl absorption band shown by the untreated humic acid at 5·85 μ. Treatment with acid or alkali has also led to decreases in transmission at wavelengths (3·45, 3·52, 6·68 and 6·95 μ) representative of absorption by aliphatic C—C single bonds. The inference to be drawn from this is that aliphatic structures have been converted into polynuclear ring systems by the action of the alkali, or into C=C double bonds conjugated with phenyl groups by the action of acid. Condensations would be expected to lead to an increased equivalent weight for the humic acid, and this has been found to be true as noted above.

Inspection of Fig. 1 makes it possible to follow the changes in pH of the individual solutions on standing. The acid solutions drift toward a higher pH, the alkaline solutions drift toward a lower pH, and there is an intermediate region

where no pronounced drift can be discerned. The pH of the solution to which 0·8 ml of acid had been added does not drift at all with time; the amount of drift decreases as the solutions approach this reaction mixture in composition.

These drifts in pH values, along with the loss of carbonyl groups noted in the infra-red spectra can be explained by several mechanisms. As an example, it is

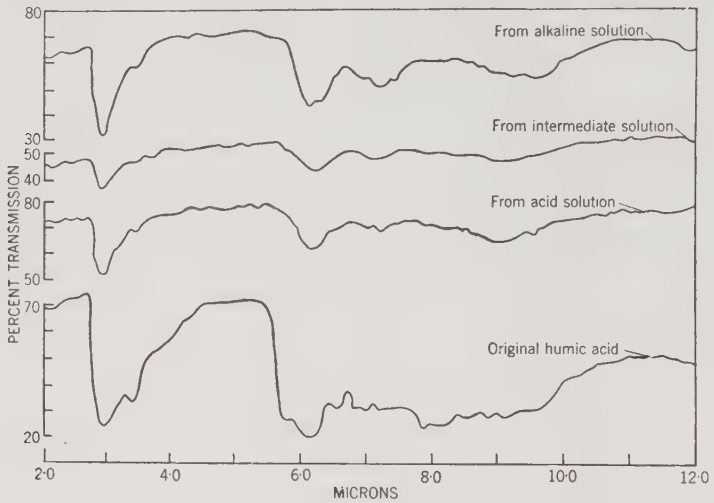
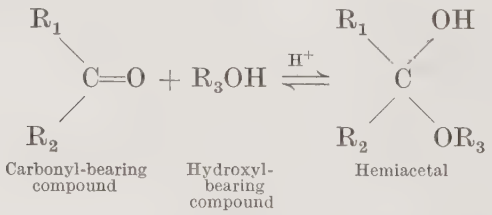


Fig. 2. Infra-red absorption spectra of humic acid recovered from alkaline solution, "intermediate" solution, and acid solution, and of original humic acid isolate

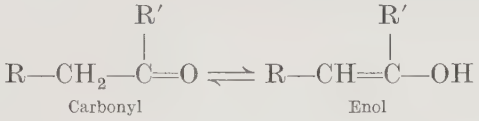
possible that carbonyl and hydroxyl groups interact to form hemiacetals in an acid environment. If the carbonyl groups were initially subject to enolization with the formation of acidic properties, acetal formation would lead to simultaneous loss of these acidic properties and of the carbonyl group. As shown in Fig. 2, the humic acid recovered from acid solution has no absorption band indicative of a carbonyl group, which apparently has completely disappeared.

Hemiacetal formation proceeds as follows:



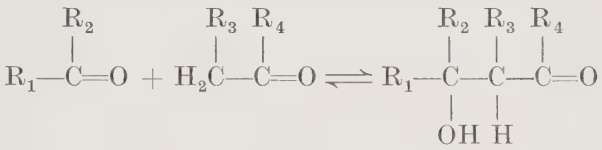
R_1, R_2, R_3 and R_4 in these and the following structures represent parts of the complex humic acid molecules. Hemiacetal formation is a reversible process. The formation of an unstable hemiacetal that would split out water to form an unsaturated ether would, moreover, result in the formation of C=C double bonds with loss of C—C single bonds noted in Fig. 2, and would also tend to drive the reaction to completion resulting in total loss of carbonyl groups.

An alkaline environment would tend to enhance the conversion of carbonyl groups into enolic structures that have acidic properties,



Under these alkaline conditions, the pH of the solution will drift toward a lower value. Enolization, however, is an equilibrium process. In this respect, the infrared spectrum for the humic acid recovered from the most alkaline solution (Fig. 2) shows a small absorption band at 5·85 μ representative of residual carbonyl groups compared to the large absorption for the untreated humic acid, and is consistent with a keto–enol equilibrium.

Absorption in the carbonyl region (5·85 μ) is also small for the intermediate solution (Fig. 2). Some condensation may have occurred but partial loss of carbonyl groups may represent incomplete reaction or perhaps equilibrium such as is found in the reversible aldol condensation which is accompanied by loss of carbonyl groups:



In aldol condensation there is no clearly defined drift in pH values which indicates no apparent change in the acidic properties of the humic acid.

Recovery of the humic acid from the alkaline (pH 9) and "intermediate" (pH 8) solutions entailed warming and was undoubtedly accompanied by increase in pH. Although these increases in pH values may have promoted aldol condensations, if such occurred, it should be remembered that the pH readings of these solutions were initially 10·3 and 9·0, and that these values decreased to 9 and 8, respectively, on standing.

Discussion and Conclusions

It is evident from this work and that which preceded it (Pommer and Breger, 1960) that humic acid can be titrated to an end-point. Moreover, based on such a titration it is possible to calculate an equivalent weight for the material. The Merck humic acid previously discussed (Pommer and Breger, 1960) was found to have an equivalent weight of 150, and the humic acid used in this work, which was isolated from a different peat, had an equivalent weight of 144 when 3 days were allowed for the attainment of equilibrium conditions before measurements were made. An important outcome of this work is the observation that the equivalent weight of the humic acid increases with time under the conditions of the experiment: 30 min after mixing it was approximately 119; 3 days afterward it was 144; and 52 days later it had reached a value of 183. It is clear, therefore, that humic acid changes in composition when permitted to stand in solution. For this reason, an equivalent weight of humic acid will have a precise meaning

only if the method by which the humic acid has been originally extracted is stated in detail; if the time and temperature under which it has been brought into solution for titration is known; and if the time between preparation and pH measurement is recorded.

It is not our purpose to cite all equivalent weights of humic acid ever reported in the literature and to comment on their divergence. Material of different origin and prepared by different means may well exhibit different equivalent weights. Unless all the factors are known it is obviously not possible to evaluate and compare such data. On the other hand, it is possible that a useful average equivalent weight for humic acid could be calculated on the basis of a series of preparations made under controlled conditions.

Acknowledgement—The assistance of J. J. Rowe in obtaining the infra-red absorption spectra is gratefully acknowledged.

References

Bateman A. M. (1951) *The Formation of Mineral Deposits.* John Wiley, New York.

Gruner J. W. (1922) The origin of sedimentary iron formations: The Biwabik formation of the Mesabi range. *Econ. Geol.* **17,** 407–460.

Harned H. S. and Owen B. B. (1958) *The Physical Chemistry of Electrolytic Solutions* (3rd Ed.). Reinhold, New York.

Kilpi S. (1943) Uber die Elektrolytwirkung bei der Säure-Basen Titration. *Ann. Acad. Sci. Fennicae* A, II, No. 10, 3–6.

Kreulen D. J. W. (1932) Studies met betrekking tot den Aanleg van Steenkool tot Broei—I. *Chem. Weekblad* **29,** 367–371.

Pommer A. M. and Breger I. A. (1960) Potentiometric titration and equivalent weight of humic acid. *Geochim. et Cosmochim. Acta.* **20,** 30–44.

Puri A. N. (1949) *Soils—Their Physics and Chemistry.* Reinhold, New York.

Rankama K. and Sahama Th. G. (1950) *Geochemistry.* University of Chicago Press, Chicago.

Thiele H. and Kettner H. (1953) Über Huminsäuren. *Kolloid-Z.* **130,** 131–160.

Geochimica et Cosmochimica Acta, 1960, Vol. 20, pp. 51 to 82. Pergamon Press Ltd. Printed in Northern Ireland

Moyens et résultats d'étude de la radioactivé due au radon dans les eaux naturelles

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Abstract—A field method for the determination of the radon content of natural waters is described, and the results obtained in the course of two surveys in different regions of France have been analysed using statistical methods. It appears that: (1) the radon contents are distributed lognormally in a given geological formation; (2) the determination of radon in waters is capable of development into a geochemical prospecting technique; (3) the radon contents of waters are very often greater than those encountered in biological systems.

Systematic studies on the determination of radon in natural waters from different geological formations have been carried out for some years (1957–1959) at the Radiogeological Research Centre at the University of Nancy. The research has essentially been directed towards the adaptation of methods for use under difficult field conditions as well as their application in very diverse regions. A certain number of results have already permitted some conclusions to be drawn (Roubault *et al.*, 1959); and the present paper continues and completes these.

Numerous methods have previously been employed for determining radon in waters, atmosphere, rocks and soils, but they are either already outmoded and slow, such as the ionisation chamber (Delibrias, 1954; currently used in the U.S.S.R. for emanometry), or necessitating fragile and delicate equipment difficult to transport from place to place in the field, such as the impulse ionisation chamber (Hudgens *et al.*, 1951).

Following the work of Damon and Hyde (1952) and of van Dilla, we have succeeded in utilising alpha-scintillation counting, with counting tubes, the inside walls of which are coated with zinc sulphide. These tubes are made of glass and comprise the measuring chamber coupled optically to a scintillation detector of the usual type; a reducing scaler completes the apparatus.

Réalisation des Récipients

Nous utilisons des ballons sphériques, en verre Pyrex, de 500 cm³ de capacité. Le fond en est légèrement concave. Sur ce fond est fixé un disque de plexiglass (44 mm de diamètre et de 8 mm d'épaisseur) de la façon suivante. Le ballon est rempli d'eau chaude à 80°–85°C puis bouché et retourné sur un support. On verse alors sur le fond concave 5 à 6 cm³ de baume du Canada amené par cuisson à sa limite de polymérisation. Le disque de plexiglass, poli sur ses deux faces, porté à une température voisine de 50°C, est posé sur le baume chaud. Les bulles d'air emprisonnées sont éliminées par pression. On laisse refroidir lentement les ballons remplis d'eau. Après refroidissement complet, les ballons sont lavés à l'eau distillée puis à l'éther éthylique pour les dégraisser soigneusement. Dans les ballons propres, on introduit une solution de graisse silicone pour vide* dans l'éther éthylique.† Cette solution très fluide est répartie uniformément sur la paroi interne du ballon. L'excès en soigneusement éliminé. L'éther, en s'évaporant, laisse sur la paroi une pellicule extrêmement résistante de graisse silicone. Cette pellicule sert de support au matériau scintillant. Celui-ci est constitué par du sulfure de zinc activé à l'argent, montrant une fluorescence bleue violette sous les impacts des α.‡ Une fenêtre est ensuite ouverte en nettoyant la partie interne du

* Graisse SISS, Société Industrielle des Silicones et Produits Chimiques du Silicum 1 bis place de Saussaies, Paris.

† 100 g de graisse SISS dans 200 cm³ d'éther éthylique.

‡ Poudre G 86, Massiot-Fluor, Ailly-le-Haut, Clocher, Somme.

ballon correspondant au disque de plexiglass. De même le col du ballon est nettoyé. La surface ainsi tapissée de sulfure de zinc représente 90% de la surface interne totale du ballon.

Les ballons ainsi confectionnés sont revêtus de deux couches de peinture blanche (émail cellulosique). Enfin, une couche de peinture noire recouvre l'ensemble. Les ballons sont alors munis d'un bouchon en caoutchouc (no. 9 ou no. 10 suivant la dimension du col) percé en son centre. Le trou reçoit un robinet à vide en verre. Les ballons numérotés sont enfermés dans un sachet de toile noire également numérotée. Ils sont enfin placés dans une caisse à casiers comportant un bourrelet anti-chocs.

Exécution des Mesures

Les mesures sont effectuées en couplant le ballon à un détecteur à scintillation.* L'ensemble est enfermé dans une enceinte étanche à la lumière. Le détecteur à scintillation est suivi de son préamplificateur mais adapté à l'ensemble de comptage.† Cette adaptation consiste en une modification des étages amplificateurs mais conserve au préamplificateur les trois valeurs du gain: 0,15, 1,5, 15.

Recherche des Conditions de Travail

Les variables, dans les conditions de travail, sont surtout liées aux ballons de mesure et à l'ensemble détecteur.

(a) *Ballons*

Le sulfure de zinc, après une longue exposition à la lumière, présente une certaine excitation et l'appareil numérateur enregistre un certain nombre d'impulsions allant en décroissant avec le temps (Fig. 1). Du fait de ce phénomène,

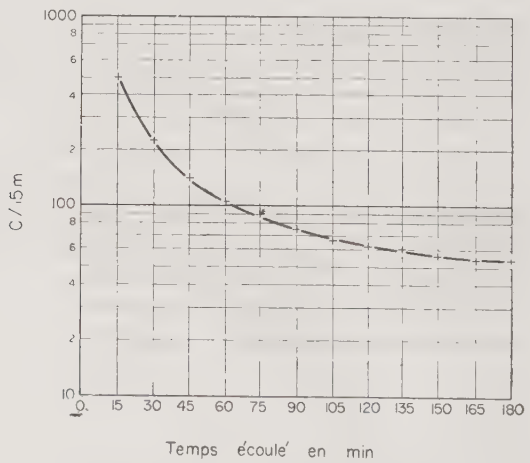


Fig. 1. Décroissance au cours du temps du nombre d'impulsions enregistrées à la suite d'une longue exposition à la lumière solaire d'un ballon de mesure.

* DCS1 Gabon (Licence C.E.A.), Lie-Belin 296, Av. Napoléon Bonaparte, Rueil, Malmaison, S. et O.
† Bloc RPN_3 comportant une échelle numératrice et une alimentation haute tension, MESCO.21, Rue René Coche, Vanves, Seine.

les ballons ont été peints d'abord en blanc (réflecteur de lumière)(KOECHLIN, 1955) puis en noir et enfin enfermés dans un sachet noir et stockés dans une caisse fermée. Les manipulations de remplissage, de changement des ballons sont effectués à l'obscurité presque complète.

Cependant, malgré toutes ces précautions, les ballons, même stockés longtemps à l'obscurité, présentent une activité faible mais mesurable, voisine de 1,15 coup/min, correspondant à une radioactivité du verre de 0,0037 α min^{-1} cm^{-2}.

(b) *Ensemble détecteur*

La détection des impulsions lumineuses dans le ballon est assurée par un photomultiplicateur* dont la photocathode est couplée optiquement au disque de plexiglass à l'aide de quelques gouttes d'huile de silicone.† Le photomultiplicateur est suivi du préamplificateur; ce dernier travaille à son gain maximum = 15, mais le gain du photomultiplicateur lui-même est une fonction de la haute tension, de la forme:

$$G = (K \,.\, V)^n$$

où G = gain;
K = constante;
V = tension interdynode;
n = nombre de dynodes.

Le gain de l'ensemble varie donc très vite avec la tension appliquée. Fig. 2 traduit cette variation dans la détection, mais à partir d'une certaine tension, apparait un "plateau". La tension de travail est toujours choisie à environ 150 V au dessus du seuil. Cette courbe est tracée avec une certaine quantité de radon

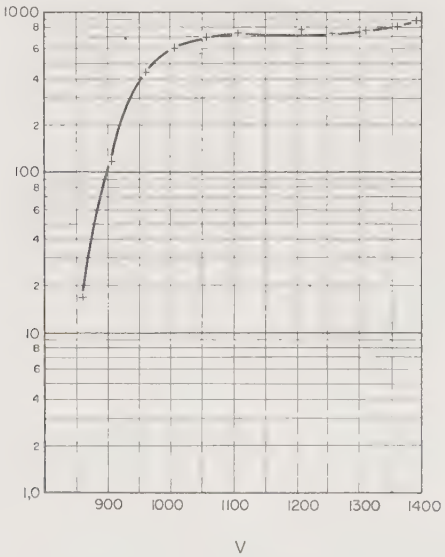


Fig. 2. Détermination de la tension de travail appliquée au photomultiplicateur (53 AVP de la Radiotechnique, no. 809). Ici la tension appliquée en cours mesure sera de 1200 V.

* Photomultiplicateur Radiotechnique 53 AVP, La Radiotechnique 130, Avenue Ledru-Rollin, Paris.
† Rhodorsil 47 V 30 000 cP, Rhône Poulenc, 21, Rue J. Goujon, Paris.

introduite dans le ballon chaque fois que l'on entreprend une série de mesures ou que l'on utilise un photomultiplicateur neuf.

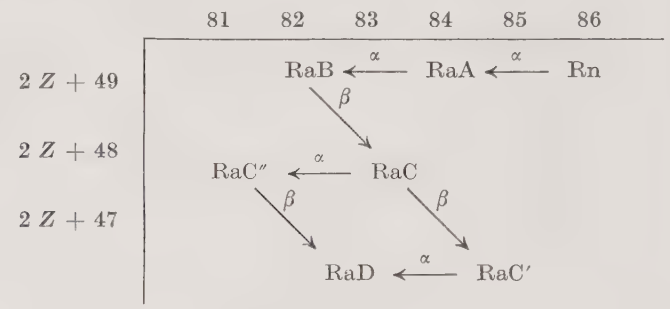
Etalonnage

Quatre sources de radium ont servi à l'étalonnage de l'ensemble de mesure. Ces sources* contiennent:

$$112{,}9 \pm 3{,}4\ \mu g \text{ de radium;}$$
$$110{,}4 \pm 3{,}31\ \mu g \text{ de radium;}$$
$$0{,}93 \pm 0{,}093 \times 10^{-4}\ \mu g \text{ de radium;}$$
$$0{,}121 \pm 0{,}012 \times 10^{-4}\ \mu g \text{ de radium.}$$

Ces sources ont servi à faire des sources d'activité plus faibles, de l'ordre de 1×10^{-10} c de radon. Le radon à doser est transféré dans le ballon suivant un processus décrit plus loin. La mesure est effectuée pendant une durée de 15 min lorsque le radon a atteint l'équilibre avec ses produits de filiation du dépôt actif au terme de 3 hr ou 3 hr 15 min. On peut chiffrer le nombre théorique de particules-α comptées pendant la mesure, au moment de l'équilibre.

Le radon émet alors 3 α suivant le schéma:



à 10^{-10} c de radon correspond donc, dans une géométrie de 4π:

$$3{,}7 \times 3\ \alpha/\text{sec}$$

Dans le cas d'une surface scintillante, la géométrie est de 2π, on ne compte de ce fait que 50% des α émis. Dans notre cas, la surface du col et la surface de la fenêtre ne sont pas sensibles. La surface revêtue de sulfure de zinc est 90–100 de la surface totale. Le nombre des α-comptés/sec pour 10^{-10} c de radon à l'équilibre est alors:

$$N/\text{sec} = \frac{3{,}7 \times 3 \times 45}{100} = 5 \text{ coups/sec, ou } 300 \text{ coups/min}$$

Nous résumons dans Tableau 1 les résultats d'étalonnage.

Remarques

(1) Il ne nous est pas paru nécessaire de contrôler par les moyens de la statistique ces deux distributions. La corrélation en effet, apparait ici très nettement.

(2) Ceci montre également qu'il n'y a pas de perte de comptage du fait de la

* Provenance, The Radiochemical Centre (UKAEA), Amersham, Buckinghamshire, Angleterre.

Tableau 1

Teneur (10^{-10} c)	Résultats calculés (coups/min)	Résultats observés* (coups/min)
0,1376 ± 10%	41 ± 4	38 ± 4
0,1525 ± 10%	45 ± 5	46 ± 5
0,1543 ± 10%	46 ± 5	42 ± 4
0,1534 ± 10%	46 ± 5	40 ± 4
0,1608 ± 10%	48 ± 5	42 ± 4
0,1785 ± 10%	53 ± 7	54 ± 5
0,3878 ± 10%	116 ± 12	103 ± 7
0,3943 ± 10%	118 ± 12	109 ± 7
0,4780 ± 10%	143 ± 14	120 ± 8
0,1424 ± 4%	43 ± 2	45 ± 4
0,1799 ± 4%	54 ± 2	53 ± 5
0,1832 ± 4%	55 ± 2	67 ± 6
0,3687 ± 4%	110 ± 4	103 ± 7
0,5685 ± 4%	170 ± 7	145 ± 8
0,1744 ± 3%	52 ± 1	40 ± 4
0,5282 ± 10%	158 ± 15	154 ± 8
3,328 ± 5%	998 ± 50	858 ± 20
0,2153 ± 3%	64 ± 2	55 ± 5

* Erreur probable établie suivant la distribution de Poisson = 0,6745 $\sqrt{N}$.

présence du baume du Canada, entre ballon et disque de plexiglass. Nous avions craint une absorption (écran jaune) des impulsions lumineuses (bleues).

(3) Enfin Tableau 1 prouve que le procédé de barbottage par vide et agitation désorbe complètement le radon de la solution du sel de radium.

Utilisation de la Méthode sur le Terrain

L'utilisation de cette méthode sur le terrain conduit à un certain nombre d'aménagements résidant surtout dans le transport et l'alimentation électrique des appareils de mesures, dans l'exécution des prélèvements d'eau et dans la désorption du radon de ces échantillons.

Transport du matériel

Il est réalisé par une camionnette 1200 kg Citroën, type H, aménagée en laboratoire (Figs. 3 et 4). Sur un flanc de la camionnette est fixée une paillasse de 1,90 m de long et de 50 cm de large, sa hauteur est de 83 cm. Un étage intermédiaire supporte les deux blocs RPN_3. A la partie inférieure sont logés une pompe à vide† et les appareils de stabilisation et de régulation du courant électrique: Alternostat et Réguvolt. Sur la partie supérieure sont fixées deux petites armoires étanches à la lumière recevant le détecteur à scintillation et possédant à l'intérieur un support réglable en hauteur permettant d'assujettir les ballons à la photocathode du photomultiplicateur. La partie arrière du véhicule est également pourvue d'une paillasse. Elle reçoit le dispositif de barbottage des échantillons. Un

† Groupe pompe à vide micropal A_2, Compagnie Générale de Radiologie 34, Boulevard de Vaugirard, Paris.

panneau d'isorel dur et une porte séparent la cabine de conduite et permet de réaliser, lorsque toutes les issues sont closes, la pénombre nécessaire aux manipulations. Enfin, le véhicule comprend un certain nombre de points de rangement: casiers, tiroirs, etc. Un câble souple permet de se raccorder au réseau électrique; d'autre part, il est prévu une mise à la terre des appareils électroniques. La

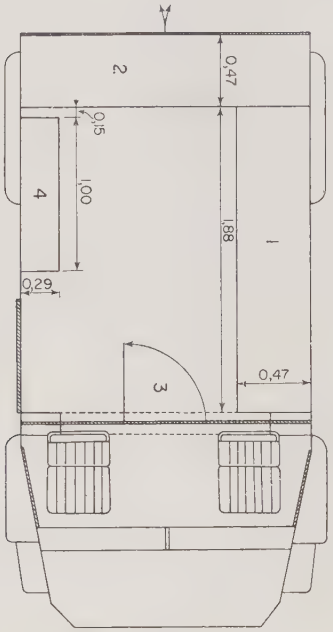


Fig. 3. Plan d'aménagement de la camionnette. (1) Chassis recevant les petites armoires. La partie inférieure supporte les blocs numérateurs RPN_3. (2) Plan de travail avec tiroirs. (3) Panneau en bois comprimé (Isorel) avec porte de communication avec la cabine de conduite. (4) Casiers de rangement. (Les cotes sont exprimées en mètres.)

solution de la génératrice n'a pas été retenu du fait de son prix de revient élevé ainsi que du fait que les points fixes sont choisis toujours en des lieux où l'on peut disposer du réseau électrique: école, hôtel, etc.

Prélèvement des échantillons d'eau

Les mesures anciennes (Delaby *et al.*, 1931) effectuées sur des sources en pays granitiques nous ont permis de calculer le volume optima d'eau à prélever.

L'activité peut osciller de 5 à 950 $\times$ 10^{-10} c/l., soit par cm^3 de 0.005 à 0,95 $\times$ 10^{-10} c, équivalent à un nombre d'α pour 15 min de comptage à l'équilibre: 18,5 à 4275. Un prélèvement de l'ordre de 25 cm^3 conduirait à une activité de 460 à 10 700 coups/15 min. De ce fait, l'erreur introduite, à cause du mouvement propre des ballons, est minime.

Réalisations des prélèvements

Les prélèvements d'eau sont exécutés de la façon suivante: des tubes à essais en verre Pyrex de 20 $\times$ 200 contenant un petit aimant enrobé, sont bouchés avec

Fig. 4. Photographie montrant la disposition du matériel dans la camionnette d'après le plan d'aménagement précédent.

un bouchon en caoutchouc bleu no. 5 ayant une forme dont la coupe est représentée ci-contre. A l'aide d'une aiguille hypodermique 35/1,5 soudée sur un mandrin de laiton de 55 mm de long et de 7 mm de diamètre, on exécute le vide dans le tube avec la pompe. L'aiguille hypodermique retirée, la plaie se referme du fait de la conformation du bouchon et la pression, à l'intérieur du tube, demeure pendant très longtemps à quelques millimètres de mercure (un tube a été conversé vidé pendant plus d'un mois).

Une seringue en verre, de 30 cm^3 de capacité, munie d'une aiguille hypodermique sert à faire le prélèvement d'eau par aspiration. L'aiguille, piquée alors dans le bouchon du tube vide d'air, permet de faire le transfert de l'eau prélevée, sans perte de gaz (Arndt et Kuroda, 1953) mais également en aidant la désorption du radon de l'eau. On note alors le lieu, l'heure et la date du prélèvement sur une petite feuille de papier collée au tube par une bande adhésive. On note également sur un carnet les conditions atmosphériques du prélèvement: température de l'air, de l'eau, pression barométrique, etc., ainsi que le lieu en coordonnées Lambert et l'altitude. La collecte des échantillons est aisée puisque le volume d'eau prélevée est faible et l'encombrement du matériel de prélèvement restreint. On peut transporter facilement de trente à trente-cinq tubes.

De retour à la camionnette-laboratoire, les tubes sont étiquetés, mis dans l'ordre des prélèvements et préparés pour le dosage du radon. Le transfert du radon dans les ballons de mesure se fait suivant une technique s'inspirant des travaux de Mache et Bamberger (in Kirsch, 1928) et de Schepotjeva (1943). Une grande aiguille hypodermique 200/1,5 est enfoncée dans le bouchon d'un tube rempli d'eau et sa partie inférieure arrive à environ 1 cm du fond. Cette aiguille est reliée par un tuyau de caoutchouc à un tube en U, contenant du charbon actif en grain et en poudre. Une aiguille hypodermique avec mandrin est alors piquée dans le bouchon, son orifice demeurant dans l'atmosphère au-dessus de l'eau du tube. Cette aiguille est raccordée à un tube en U contenant un desséchant (perchlorate de magnésium) lui-même en relation avec un ballon de mesure où le vide a été exécuté à l'aide de la pompe. Par le jeu des robinets, on effectue un barbottage d'air se chargeant du radon au cours de son passage dans l'eau. Le débit d'air est réglé de telle sorte que le remplissage du ballon se fasse en 15 min. L'installation est complétée par un agitateur électromagnétique provoquant le déplacement du barreau aimanté du tube parachevant ainsi la désorption du radon. Le ballon rempli d'air et de radon est alors placé dans la caisse à casiers, la mesure étant effectuée 3 hr 15 min après la fin du barbottage.

La teneur en radon est obtenue en utilisant la formule suivante (pour un temps de comptage de 15 min et un volume d'eau de 30 cm^3):

$$\text{Rn } 10^{-10} \text{ c/l.} = \frac{N - n}{135 \times \tau}$$

où N est le nombre total de coups enregistrés en 15 min;

n le nombre de coups correspondant au mouvement propre du ballon de mesure pendant le même temps;

τ un nombre plus petit que un, réalisant une correction introduite du fait

qu'entre le moment du prélèvement et celui de la mesure une partie du radon de l'eau a disparu par désintégration.*

En établissant judicieusement barbottage et mesures, il est possible d'exécuter de vingt à trente dosages par jour.

Résultats

Ainsi mise au point, la méthode a été appliquée sur le terrain au cours des étés 1958 et 1959. Les régions visitées sont les Vosges méridionales, la Vendée et la Bretagne. Nous grouperons ici les résultats des diverses campagnes et nous tenterons de dégager les faites nouveaux qui semblent apparaitre.

Campagne 1958:

Vosges. La campagne s'est déroulée au flanc sud de la Vallée de la Moselle, depuis le Ballon de Servance jusqu'au col du Mont de Fourche. Les sources, où les eaux ont été prélevées, naissent toutes sur le granite. Les teneurs rangées par classes logarithmiques se distribuent de la façon suivante (Tableau 2).

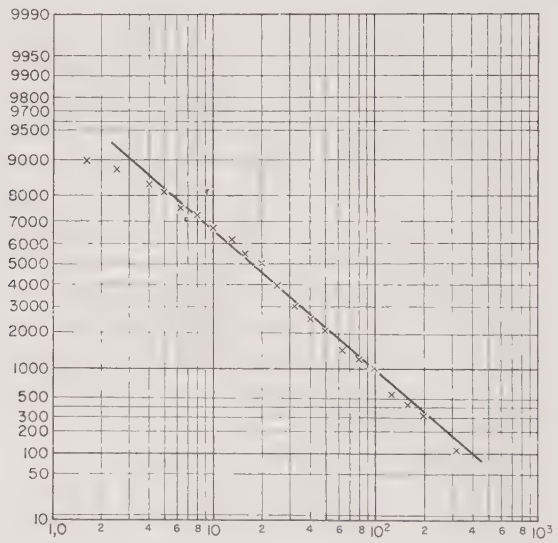


Fig. 5. Ajustement graphique concernant les valeurs obtenues dans les Vosges en 1958.

Ces différentes valeurs portées sur un papier logarithmique gaussien permettent d'obtenir un certain nombre de points alignés. L'ajustement graphique à la loi lognormale est excellent (Fig. 5).

Vendée. Les mesures ont été exécutées sur le massif granitique au sud-est de Mortagne-sur-Sèvre. Ce massif a été étudié en détail lors des prospections exécutées

* Une table a été établie pour obtenir aisément ce nombre l'équation de destruction du radon

$$Q = Q_0 e^{-\lambda t}$$

où Q_0 = quantité initiale de radon; e = base logarithme népérien; λ = constante de désintégration du radon; t = temps, a servi aux calculs.

Tableau 2

Teneur (10^{-10} c/l.)	Nombre	Pourcentage	Fréquence cumulée	F.C. × 100
1,58	9	10	—	—
2	2	2,22	90,00	9000
2,5	0	—	—	—
3,2	4	4,45	87,76	8776
4	2	2,22	83,31	8331
5	5	5,55	81,09	8109
6,3	3	3,33	75,54	7554
8	4	4,45	72,21	7221
10	6	6,66	67,76	6776
12,6	5	5,55	61,10	6110
15,8	5	5,55	55,55	5555
19,9	9	10	50,00	5000
25,1	5	5,55	40,00	4000
31,6	4	4,44	34,45	3445
39,8	4	4,44	30,00	3000
50,1	4	4,44	25,54	2554
63,1	6	6,66	21,10	2110
79,4	2	2,22	14,44	1444
100	2	2,22	12,22	1222
126	4	4,44	10	1000
158	1	1,11	5,55	555
199	1	1,11	4,44	444
251	2	2,22	3,33	333
316	0	—	—	—
398	1	1,11	1,11	111
	90			

par le CEA pour recherche d'uranium. La bande couverte se superpose à celle étudiée par le Centre en vue de reconnaître la distribution de la teneur en U du Massif. La première campagne n'a pas dépassé la route nationale N 148 bis de Nantes à Poitiers. Tableau 3 rassemble les résultats de la campagne.

Reportées sur le papier logarithmique gaussien, les valeurs permettent d'obtenir une droite qui se brise aux environs de 150 × 10^{-10} c/l. (Fig. 6). Nous essayerons de dégager plus loin la signification de cette solution de continuité.

Tableau 3

Teneur (10^{-10} c/l.)	Nombre	Pourcentage	Fréquence cumulée	F.C. × 100
1,58	2	1,96	—	—
2	1	0,98	96,88	9688
2,5	1	0,98	95,9	9590
3,2	3	2,74	94,92	9492
4	0	—	—	—
5	0	—	—	—
6,3	1	0,98	92,08	9208
8	4	3,92	91,10	9110
10	1	0,98	87,18	8718
12,6	1	0,98	86,20	8620
15,8	2	1,96	85,22	8522
19,9	5	4,90	83,26	8326
25,1	2	1,96	78,36	7836
31,6	6	5,88	76,4	7640
39,8	5	4,90	70,52	7052
50,1	9	8,82	65,62	6562
63,1	4	3,92	56,80	5680
79,4	7	6,86	52,88	5288
100	1	0,96	46,02	4602
126	3	2,93	44,04	4404
158	8	7,84	42,10	4210
199	9	8,82	35,26	3526
251	5	4,90	26,44	2644
316	5	4,90	22,54	2254
398	9	8,82	17,64	1764
501	2	1,96	8,82	882
631	0	—	—	—
794	2	1,96	6,86	686
1000	3	2,94	4,90	490
1260	1	0,98	1,96	196
	1	0,98	0,98	98
	102			

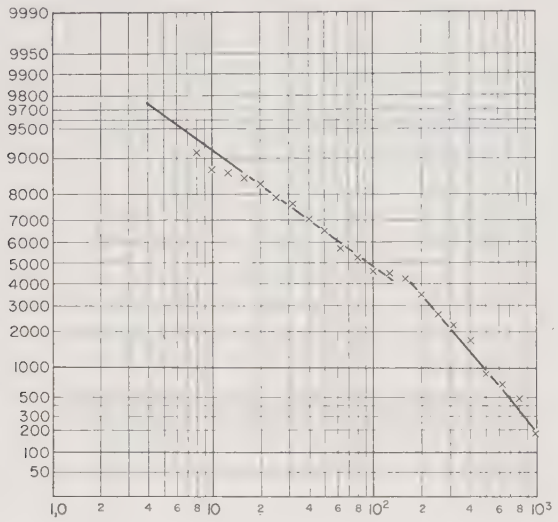


Fig. 6. Ajustement graphique concernant les résultats de Vendée en 1958.

Bretagne. En 1958 les mesures de radon ont été exécutées dans la région de Questembert, Limerzel, Tré à l'Est de Vannes, Morbihan. Les eaux des sources et des puits proviennent de deux formations géologiques. Ceci nous conduira à séparer les résultats concernant cette région.

L'ajustement graphique bien qu'imparfait est satisfaisant (Fig. 7).

Dans ce cas encore l'ajustement graphique est satisfaisant (Fig. 8).

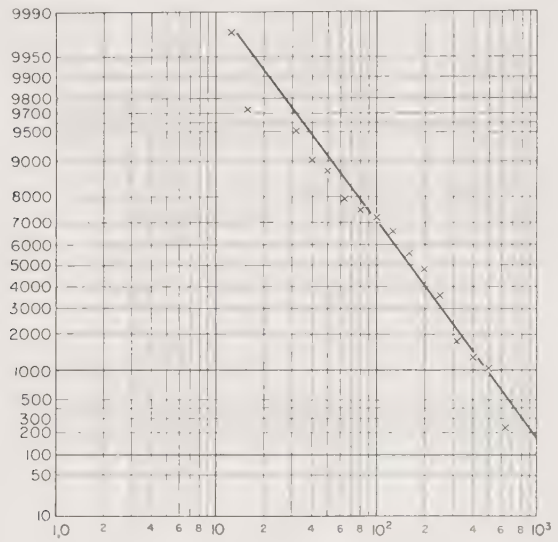


Fig. 7. Ajustement graphique des résultats concernant la granulite de la région de Questembert (Bretagne) 1958.

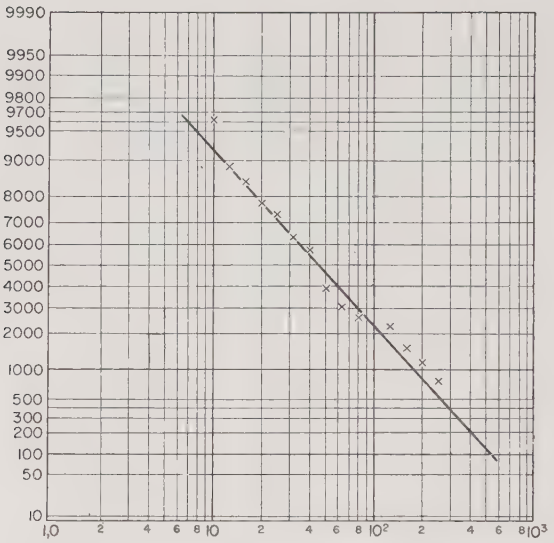


Fig. 8. Ajustement graphique des résultats concernant les résultats des micaschistes et des gneiss de la région de Questembert.

Campagne de 1959

Vosges. Les prélèvements au cours de cette campagne ont été exécutés sur des eaux provenant du granite et des grès. Les résultats respectifs sont consignés dans Tableaux 6 et 7.

L'ajustement graphique est parfait, mais la droite se brise aux environs de 95×10^{-10} c/l. (Fig. 9).

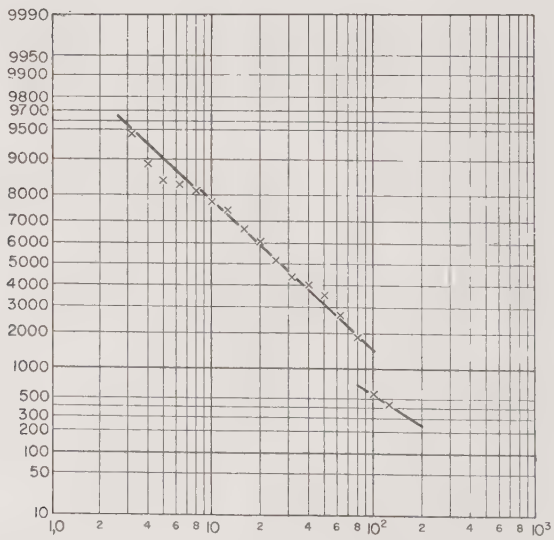


Fig. 9. Ajustement graphique concernant les résultats obtenus sur les eaux issues du granite. Vosges 1959.

Tableau 4. Zone de la granulite

Teneur (10^{-10} c/l.)	Nombre	Pourcentage	Fréquence cumulée	F.C. × 100
1,58	1	2,3	—	—
2	—	—	—	—
2,5	—	—	—	—
3,2	—	—	—	—
4	—	—	—	—
5	—	—	—	—
6,3	—	—	—	—
8	—	—	—	—
10	—	—	—	—
12,6	1	2,3	99,85	9985
15,8	1	2,3	97,55	9755
19,9	—	—	—	—
25,1	—	—	—	—
31,6	2	4,8	95,25	9525
39,8	1	2,4	90,45	9045
50,1	4	8,15	88,05	8805
63,1	2	4,8	79,9	7990
79,4	1	2,4	75,1	7510
100	3	6,1	72,7	7270
126	5	10,2	66,6	6660
158	4	8,15	56,4	5640
199	6	12,2	48,25	4825
251	9	18,3	36,05	3605
316	2	4,8	17,75	1775
398	2	4,8	12,95	1295
501	4	8,15	10,55	1055
631	1	2,4	2,4	240
794	—	—	—	—
	49			

Tableau 5. Zone des gneiss et des micaschistes

Teneur (10^{-10} c/l.)	Nombre	Pourcentage	Fréquence cumulée	F.C. × 100
1,58	1	3,85	—	—
2	—	—	—	—
2,5	—	—	—	—
3,2	—	—	—	—
4	—	—	—	—
5	—	—	—	—
6,3	—	—	—	—
8	2	7,7	96,25	9625
10	1	3,85	88,55	8855
12,6	2	7,7	84,7	8470
15,8	1	3,85	77,00	7700
19,9	1	3,85	73,15	7315
25,1	2	7,7	69,3	6930
31,6	1	3,85	61,60	6160
39,8	5	19,25	57,75	5775
50,1	2	7,7	38,5	3850
63,1	1	3,85	30,80	3080
79,4	1	3,85	26,95	2695
100	0	—	—	—
126	2	7,7	23,10	2310
158	1	3,85	15,40	1540
199	1	3,85	11,55	1155
251	2	7,7	7,7	770
316	—	—	—	—
	26			

Tableau 6. Granite

Teneur (10^{-10} c/l.)	Nombre	Pourcentage	Fréquence cumulée	F.C. × 100
1,58	4	5,65	—	—
2	4	5,65	94.45	9445
2,5	0	—	—	—
3,2	3	4,23	88,79	8879
4	0	—	—	—
5	1	1,41	84,56	8456
6,3	1	1,41	83,15	8315
8	3	4,23	81,74	8174
10	2	2,82	77,51	7751
12,6	6	8,45	74,69	7469
15,8	4	5,65	66,24	6624
19,9	7	9,86	60,59	6059
25,1	5	7,05	50,73	5073
31,6	3	4,23	43,68	4368
39,8	3	4,23	39,45	3945
50,1	6	8.45	35,22	3522
63,1	6	8,45	26,77	2677
79,4	7	9,86	18,32	1832
100	2	2,82	8,46	846
126	1	1,41	5,64	564
158	3	4,23	4,23	423
	71			

Tableau 7. Grès

Teneur (10^{-10} c/l.)	Nombre	Pourcentage	Fréquence cumulée	F.C. × 100
1,58	1	11,6	—	—
2	6	—	—	—
2,5	6	6,32	88,53	8853
3,2	11	11,6	82,21	8221
4	8	8,42	70,61	7061
5	14	14,75	62,19	6219
6,3	4	4,21	47,44	4744
8	7	7,37	43,23	4323
10	10	10,5	35,86	3586
12,6	8	8,42	25,36	2536
15,8	7	7,37	16,94	1694
19,9	3	3,16	9,57	957
25,1	3	3,16	6,41	641
31,6	0	—	—	—
39,8	2	2,10	3,25	325
50,1	1	1,15	1,15	115
	95			

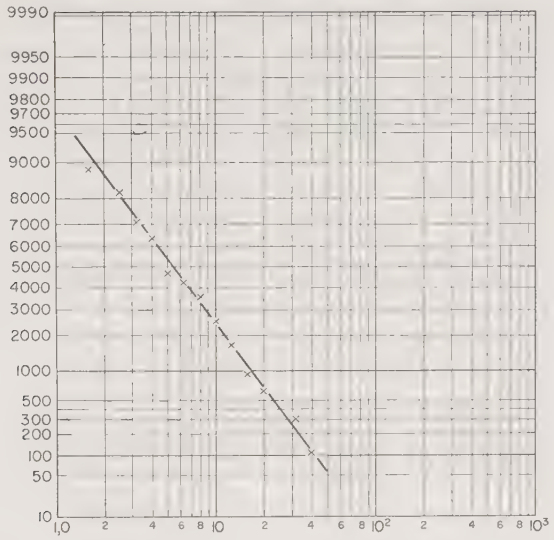


Fig. 10. Ajustement graphique des valeurs concernant les eaux des grès. Vosges 1959.

L'ajustement graphique est ici excellent (Fig. 10). Les paramètres que l'on peut en tirer seront étudiés plus loin.

Vendée. La campagne s'est déroulée au nord de la route de Nantes à Poitiers (Tableau 8).

La droite représentant cette distribution se brise aux environs de 120–130 $\times$ 10^{-10} c/l. (Fig. 11).

Enfin la dernière partie de la campagne s'est déroulée dans la région de Pontivy.

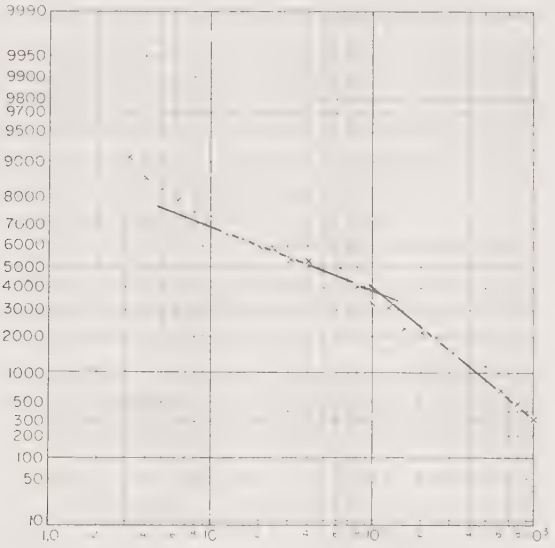


Fig. 11. Ajustement graphique des valeurs concernant les résultats de Vendée 1959.

Tableau 8

Teneur (10^{-10} c/l.)	Nombre	Pourcentage	Fréquence cumulée	F.C. × 100
1,58	5	8,2		
2	1	1,64	92,58	9258
2,5	0	—	—	—
3,2	0	—	—	—
4	3	4,92	90,94	9094
5	2	3,28	86,02	8602
6,3	2	3,28	82,74	8274
8	3	4,92	79,46	7946
10	1	1,64	74,54	7454
12,6	5	8,2	72,9	7290
15,8	1	1,64	64,7	6470
19,9	2	3,28	63,06	6306
25,1	1	1,64	59,78	5978
31,6	3	4,92	58,14	5814
39,8	1	1,64	53,12	5312
50,1	2	3,28	52,48	5248
63,1	0	—	—	—
79,4	5	8,2	49,2	4920
100	5	8,2	41,0	4100
126	1	1,64	32,80	3280
158	5	8,2	31,16	3116
199	1	1,64	22,96	2296
251	1	1,64	21,32	2132
316	3	4,92	19,68	1968
398	2	3,28	14,76	1476
501	0	—	—	—
631	3	4,92	11,48	1148
794	1	1,64	6,56	656
1000	1	1,64	4,92	492
1260	1	1,64	3,28	328
1580	0	—	—	—
1996	1	1,64	1,64	164
	61			

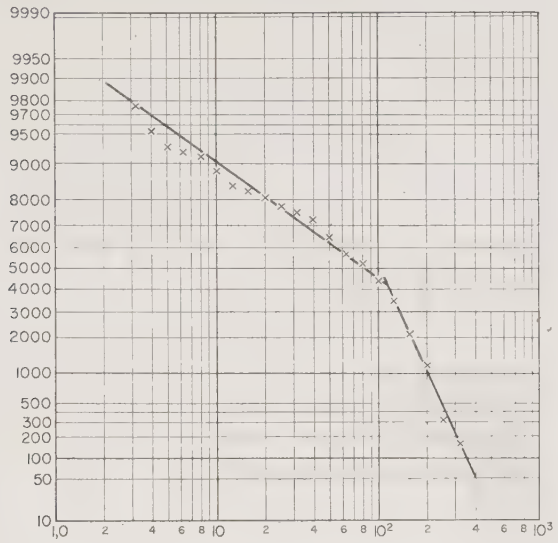


Fig. 12. Ajustement graphique concernant les résultats obtenus sur la granulite de Pontivy (Bretagne) 1959.

Les eaux ont été prélevées dans des sources ou des puits rencontrés soit sur la granulite, soit sur les schistes plus ou moins métamorphiques. Tableaux 9 et 10 tiennent comptent de cette localisation.

La représentation graphique de cette distribution conduit dans le cas de la granulite à une droite se brisant aux alentours de 120–125 $\times$ 10^{-10} c/l. (Fig. 12); tandis que l'ajustement graphique concernant les schistes est très satisfaisant. (Fig. 13).

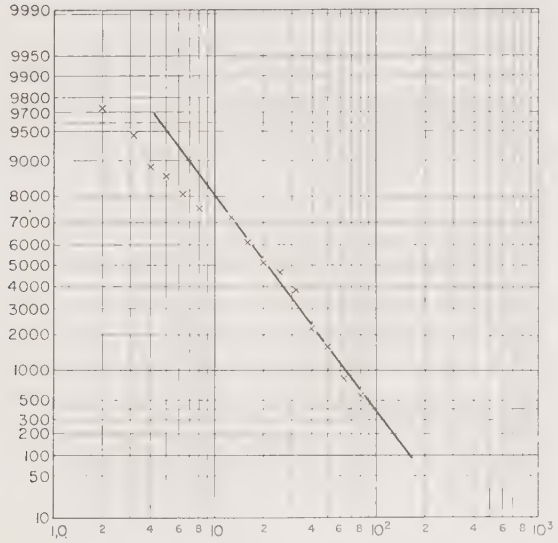


Fig. 13. Ajustement graphique concernant les résultats obtenus sur les schistes de la région de Pontivy 1959.

Tableau 9. Granulite

Teneur (10^{-10} c/l.)	Nombre	Pourcentage	Fréquence cumulée	F.C. × 100
1,58	—	—	—	—
2	2	1,6	99,2	9920
3,2	3	2,4	97,6	9760
4	3	2,4	95,2	9520
5	1	0,8	92,8	9280
6,3	1	0,8	92,0	9200
8	3	2,4	91,2	9120
10	1	0,8	88,8	8880
12,6	5	4	88,0	8800
15,8	2	1,6	84,0	8400
19,9	2	1,6	82,4	8240
25,1	4	3,2	80,8	8080
31,6	3	2,4	77,6	7760
39,8	3	2,4	75,2	7520
50,1	10	8	72,8	7280
63,1	9	7,2	64,8	6480
79,4	6	4,8	57,6	5760
100	11	8,8	52,8	5280
126	11	8,8	44,0	4400
158	17	13,6	35,2	3520
199	13	9,5	21,6	2160
251	11	8,8	12,0	1200
316	2	1,6	3,2	320
398	2	1,6	1,6	160
	125			

Tableau 10. Schistes métamorphiques

Teneur (10^{-10} c/l.)	Nombre	Pourcentage	Fréquence cumulée	F.C. × 100
1,58	1	2,78	—	—
2	1	2,78	97,22	9722
3,2	2	5,56	94,44	9444
4	1	2,78	88,84	8884
5	2	5,56	86,06	8606
6,3	2	5,56	80,5	8050
8	1	2,78	74,94	7494
10	0	—	—	—
12,6	4	11,1	72,16	7216
15,8	2	5,56	61,06	6106
19,9	3	8,3	55,5	5550
25,1	3	8,3	47,2	4720
31,6	6	16,7	38,9	3890
39,8	2	5,56	22,2	2220
50,1	3	8,3	16,64	1664
63,1	1	2,78	8,34	834
79,4	2	5,56	5,56	556
100	—	—	—	
	36			

Rappelons ici que, dans le cas d'un ajustement graphique, on se sert surtout des points voisins de l'axe 50%.

Parametres Deduits de l'étude des Droites et leur Signification

Tableau 11 rassemble les caractéristiques des distributions étudiées (Leveau, 1957).

Massif Vosgien

Ce tableau fait apparaitre que dans le massif vosgien environ 27% des points d'eau visités en 1958 atteignent ou dépassent la dose de tolérance: 40×10^{-10} c/l. (Combrisson, 1955). Dans cette même région on aura 95 chances sur 100 de se trouver en présence d'une anomalie de teneur en radon lorsqu'elle dépasse 175×10^{-10} c/l. Les sources dont les teneurs dépassent cette valeur sont au nombre de cinq. Par teneurs croissantes ce sont:

	Situations géographiques coordonnées Lambert		
(1) Source écarts du Hameau de la Pile	200×10^{-10} c/l.	424–550	113–920
(2) Source de l'Ecole de la Pile	203×10^{-10} c/l.	424–100	114–900
(3) Source dans une carrière de granite (St. Blaise)	218×10^{-10} c/l.	426–700	112–040
(4) Source chemin des Landres à la Verrerie	330×10^{-10} c/l.	426–880	113–160
(5) Source La Fonderie au dessus du km 7	380×10^{-10} c/l.	429–920	115–900

Dans les environs des deux sources de la Pile (1 et 2) on note les valeurs suivantes de teneur en uranium du granite:

10 p.p.m.	424–050	113–960
16,5 p.p.m.	424–940	114–100
12 p.p.m.	424–200	114–940

Quant à la source no. (3) on relève:

8 p.p.m.	426–700	112–040
15 p.p.m.	426–010	112–060

La suivante (no. 4) est intéressante du fait qu'une anomalie de teneur en uranium dans les eaux a été trouvée dans son voisinage (Rapport CEA inédit, Campagne hydrogéochimique, Vosges, 1957).

Enfin la dernière, bien que les teneurs en uranium du granite environnant présente des teneurs voisines de $6{,}5 \times 10^{-6}$ g/g, doit retenir l'attention. En effet, très près de ce point la même mission ayant été établie le rapport cité ci-dessus a noté une anomalie très forte de teneur en uranium dans l'eau et dans les alluvions (prélèvement no. 449).

Questembert macaschistes et gneiss

Les teneurs ici sont notablement plus faibles que pour la granulite. Cependant 67% des sources et des puits ont des teneurs au moins égales ou supérieures à la

Tableau 11

	γ, médiane ($\times 10^{-10}$ c/l.)	m, moyenne ($\times 10^{-10}$ c/l.)	σ, écart type logarithmique	σ^2, variance logarithmique	2σ, logarithmique	2σ, valeur arithmétique ($\times 10^{-10}$ c/l.)	Anomalies-95% ($\times 10^{-10}$ c/l.)	Pourcentage supérieur à 40^{-10} c/l. (%)
Vosges (granite) 1958	18	44	1,36	1,85	2,72	131	175	27
Questembert (granite)	160	235	0,87	0,75	1,74	59	295	94
Questembert micaschistes et gneiss	45	78	1,07	1,15	2,14	85	163	67
Pontivy schistes	21	31	0,89	0,8	1,78	59	90	22
Vosges grès	5,5	8	0,89	0,8	1,78	59	67	1
Vendée 1958	Cassure	150						75
Vendée 1959	Cassure	120						52
Vosges 1959 granite	Cassure	95						40
Pontivy granulite 1959	Cassure	120						66

dose de tolérance. On peut considérer comme anomalie les teneurs dépassant 165×10^{-10} c/l.

	($\times 10^{-10}$ c/l.)
(1) Carnely	193
(2) Kerantal	224
(3) Kerdin	264
(4) Kergonadan	282

Le premier et le troisième point d'eau sont situés en plein massif de gneiss granulitique tandis que le second et le quatrième sont situés très près du contact des micaschistes avec la granulite. Comme précédemment la comparaison avec les résultats des autres prospections est souhaitable.

Pontivy—Schistes

Les teneurs sont à rapprocher de celles obtenues dans les Vosges 1958; 22% des sources ou des puits ont une teneur supérieure à 40×10^{10} c/l. et une seule source a 95 chances sur 100 d'être une anomalie:

Source Sud de Pontivy, 96×10^{-10} c/l.

Cette source se trouve être au contact schiste–granulite. Cette position expliquerait alors la teneur élevée en radon.

Vosges (grès)

La moyenne (abondance géochimique) est faible au regard des teneurs reconnues dans les eaux d'autres formations géologiques et ici seulement une source sur 100 atteint la dose de tolérance et aucune source ne peut être considérée comme une anomalie.

Toutes les distributions précédentes ont un ajustement graphique parfait et la droite ne présente pas de cassure. Il n'en est pas de même dans les distributions suivantes qui, sauf une, concernent des massifs *possèdant des gîtes uranifères.*

Région de Questembert

Les eaux de sources et de puits de la zone granulitique ont des teneurs très élevées et ici 94% des eaux étudiées ont des teneurs supérieures à 40×10^{-10} c/l. De plus estimant qu'au delà de 295×10^{-10} c/l. on aura 95 chances sur 100 de se trouver en présence d'une anomalie, on relève alors dix valeurs correspondant aux sources suivantes:

	($\times 10^{-10}$ c/l.)
Kervran	297
Montaigu	342
Brunelay	380
Le Boulin	448
Grée aux chevaux	455
Bois des plats	540
Lavoir (44,7—77,2)	
Le Sourd	548
Ferme de Coët Drot	580
Limerzel	604
Coët Bihan	765

Sept de ces points d'eau, Montaigu, Limerzel, Brunelay, Le Boulin, La Grée aux Chevaux, Le Sourd et Coët Bihan, se trouvent situés au contact ou très près du contact entre la granulite et les micaschistes ou les gneiss. Deux seulement, Coët-Drot et Le Bois des Plats, sont situés au coeur de la formation granulitique, enfin, le dernier, Kervran, est situé au contact de la granulite et d'un filon de quartz.

Nous ne connaissons aucun des résultats de prospection qui ont été exécutés par le CEA dans cette région; cependant nous croyons savoir que le BRGGM aux cours de prospections pour étain, a noté la présence de monazite dans cette région. Il serait très intéressant de pouvoir confronter les localisations géographiques de ces gisements.

Vendée 1958

Des points d'eau visités 75% ont une teneur supérieure ou égale à la dose de tolérance et 42% ont une teneur supérieure à 150×10^{-10} c/l. (point de la cassure de la droite). Si l'on reporte sur la carte ces points d'eau (Fig. 14a) on s'aperçoit qu'ils coïncident avec les zones plus ou moins minéralisées reconnues en affleurements (Sanselme et Gerstner, 1958) (Fig. 14b).

Vendée 1959

Comme dans la distribution précédente on observe une cassure se produisant à 120×10^{-10} c/l. et de ce fait 35% des points d'eau visités révèlent une teneur supérieure à cette valeur, 52% montrant une teneur supérieure à la dose de tolérance. En reprenant la répartition géographique comme précédemment, on retrouve les zones d'affleurements uranifères. Si ce même travail est exécuté sur la carte de levés géochimiques (Fig. 15a) la coïncidence devient plus frappante encore (Fig. 15b) (Grimbert, 1957).

Vosges—granite 1959

L'ajustement graphique est parfait, 40% des sources présentent une teneur au moins égale à la dose de tolérance. Quelques valeurs se détachent nettement de la droite à partir de 95×10^{-10} c/l. Il s'agit de quelques sources tièdes utilisées par les thermes de Plombières:

Savonneuse no. 4, 97×10^{-10} c/l.
Savonneuse no. 5, 100×10^{-10} c/l.

et d'eaux froides de la vallée de Plombières:

Source de la gare, 131×10^{-10} c/l.
Source Yoccope, 141×10^{-10} c/l.

et d'une source du flanc est de la Vallée de Corravillers:

Bertincote, 137×10^{-10} c/l.

Pontivy—granulite

La droite présente une cassure comme celle de Vendée (1959) à 120×10^{-10} c/l. —40% des points d'eaux présentent des teneurs supérieures à cette valeur et 66% des sources ont une teneur au moins égale à 40×10^{-10} c/l. Ne possèdant actuellement que peu de renseignements sur cette région nous ne pouvons qu'utiliser les données de la carte géologique.

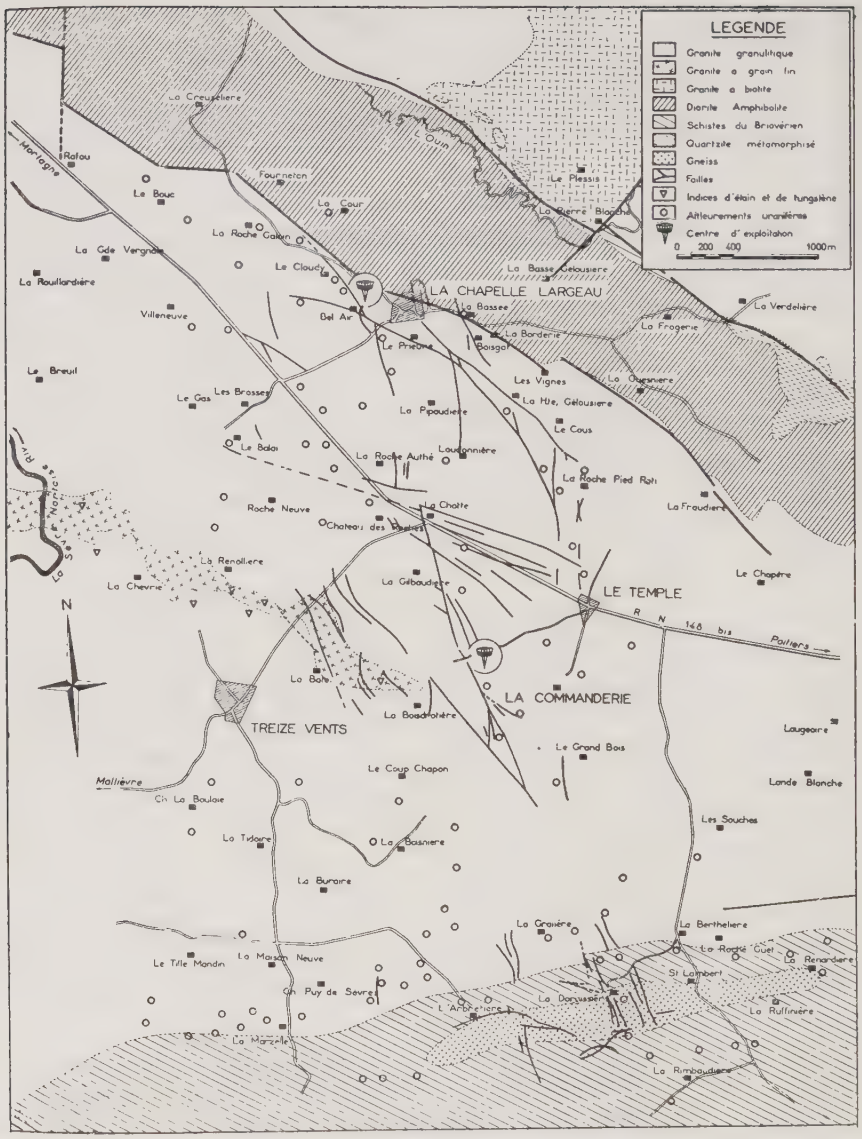


Fig. 14(a). Affleurements uranifères reconnus dans la région de La Chapelle Largeau et de la Commanderie (d'après Sanselme et Gerstner, 1958).

Les points d'eau ou groupe de sources voisines se répartissent de la façon suivante: quinze au centre du massif; dix au contact de la granulite et des schistes métamorphiques et cinq voisins de la zone minéralisée de la région de Guern (Fig. 16).

Conclusion

Les apports de cette étude dans la connaissance de la géochimie de l'U sont de trois ordres: théorique, pratique et biologique.

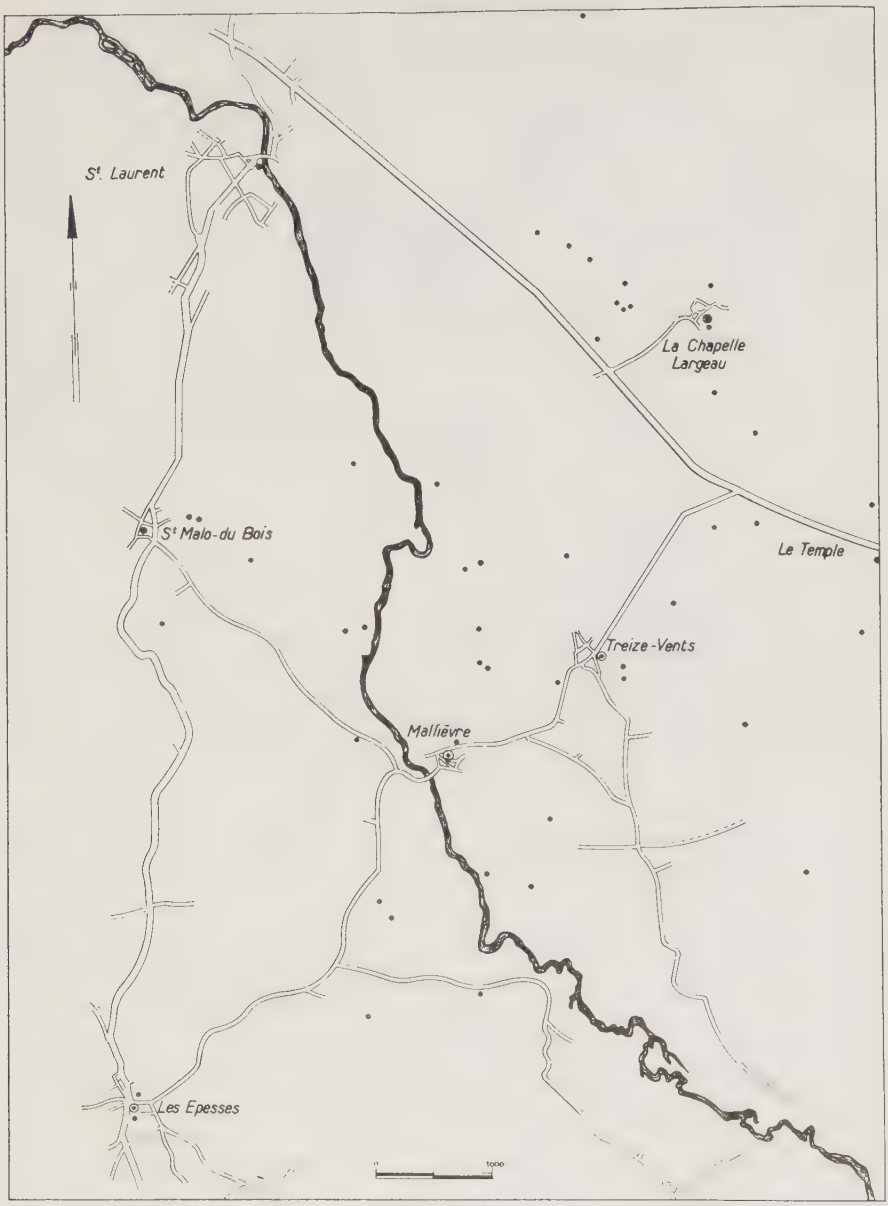


Fig. 14(b). Distribution géographique des anomalies de teneur en radon des eaux d'une partie de la région représentée en 14(a). Comparer les distributions des anomalies de radon dans les eaux et des affleurements uranifères.

1. *Théorique*

Les teneurs en radon des eaux naturelles d'une formation géologique homogène se distribuent lognormalement. La moyenne de cette distribution (abondance géochimique) reflète la teneur en élément de la famille U de la formation géologique envisagée (Jurain, 1958). Par exemple les grès du Trias inférieur des Vosges qui

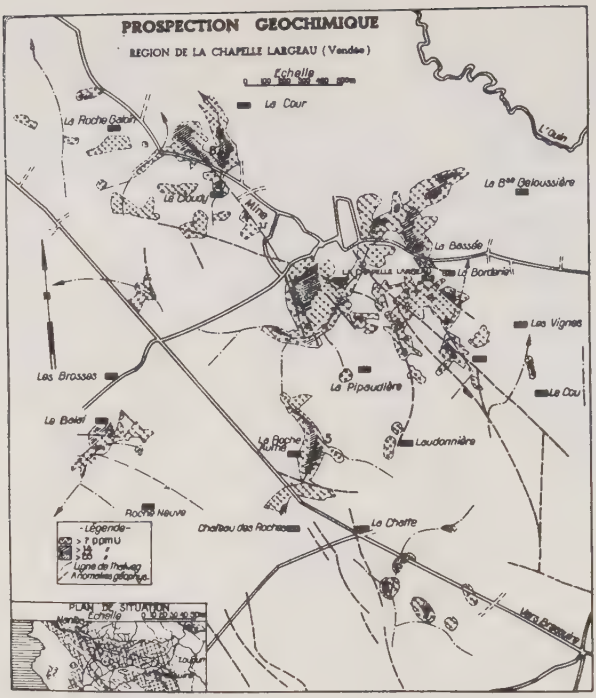


Fig. 15(a). Carte des levés géochimiques concernant l'Uranium dans les sols, région de La Chapelle-Largeau (Vendée) (d'après GRIMBERT, 1957).

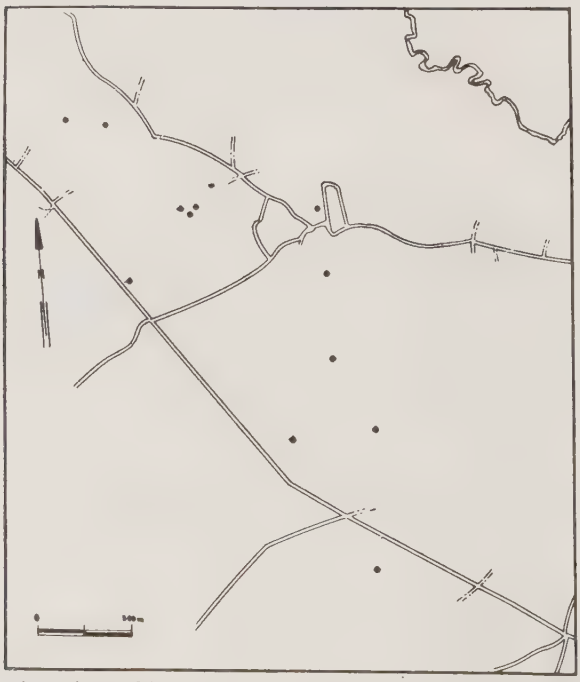


Fig. 15(b). Situation géographique des anomalies de radon dans les eaux; région de La Chapelle-Largeau (Vendée). Comparer avec Fig. 15(a).

ont des teneurs en uranium faible (des échantillons de ces grès prélevés suivant une maille kilométrique ont été analysés; les résultats en seront publiés ultérieurement) et leur activité-γ peu élevée, possèdent des sources dont les teneurs en radon sont faibles par rapport au granite sous-jacent.

2. *Pratique*

Découlant du fait théorique ci-dessus, le dosage du radon va permettre de mettre en évidence les anomalies de teneur en éléments de la famille U—R_a. Les

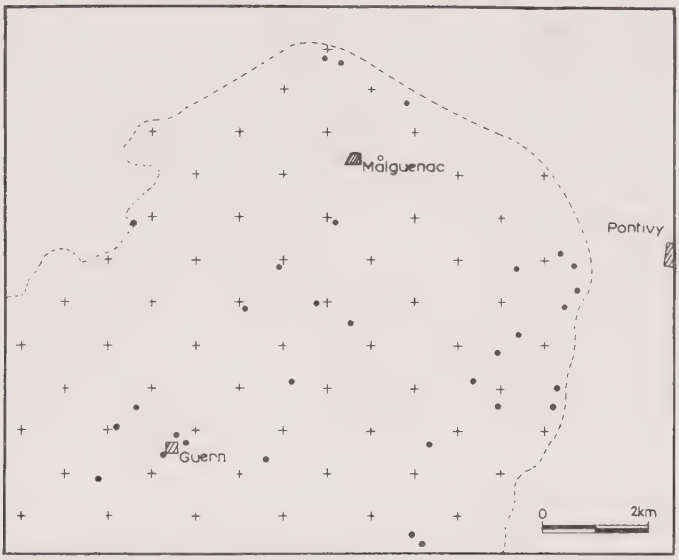


Fig. 16. Distribution géographique des sources dont les tenevrs en radon sont anormales dans le massif de granulite de Pontivy, Bretagne.

études exécutées sur les Vosges en 1958, en Vendée et en Bretagne sont particulièrement encourageants. Il semble donc que le dosage du radon dans les eaux puisse être utilisé en prospection de la famille U.

Mais avant d'inclure cette technique dans l'arsenal des méthodes de prospection, il convient d'en éprouver encore la validité et également d'en considérer les qualités (Bernard *et al.*, 1959). Or, ce que l'on demande à une méthode de prospection sont sensibilité, rapidité et faible prix de revient.

Les teneurs en radon de l'ordre de 10^{-10} c/l. sont aisément décelables. La vitesse d'avancement relativement importante: deux opérateurs peuvent exécuter aisément de vingt-cinq à trente analyses (prélèvements compris) par jour représentant une surface variable avec la densité des points d'eau mais de l'ordre de 6 à 7 km^2. Le prix de revient global (transport, prélèvement, amortissement de véhicules et de matériel) d'une analyse est voisin de 1000 Fr (10 NF). Ceci représenterait une dépense moyenne de 4000 à 5000 Fr (40 à 50 NF) par km^2.

Tant par ses résultats que par son prix de revient, cette technique peut s'inscrire entre la prospection stratégique c'est-à-dire tendant à circonscrire des zones susceptibles de renfermer une minéralisation et la prospection tactique ayant pour

but de déceler le corps minéralisé lui-même. Ajoutons enfin que la teneur en radon elle-même semblerait liée à l'importance de la minéralisation.

Il semble donc que nous apportons un élément positif dans le problème de l'utilisation possible du dosage du radon dans les eaux naturelles en vue de la prospection de l'uranium.

Cette possibilité, entrevue par Kuroda *et al.*, (1954), rejetée par Coulomb (1955), admise implicitement par Pradel (1956) ainsi que par Stead (1955,1958), ne semble pas avoir fait l'objet d'études plus poussées.

Cependant la teneur en Radon de l'atmosphère du sol (Budde, 1956) ou des sondages a servi de moyen de prospection (Stead, 1955, 1958, Tanner, 1958) et dans d'autres cas il est possible que la mesure du radon dans les eaux naturelles ait été utilisée (U.R.S.S., Pologne)(Grammakov *et al.*, 1958; Dormois *et al.*, 1959).

Le radon dissout dans l'eau constituerait donc un traceur de l'uranium. Les résultats obtenus dans les sondages par Hilpert et Bunker (1957), illustrent parfaitement ce fait et corroborent les résultats que nous avons exposés.

3. *Biologique*

Dans une note précédente (Roubault *et al.*, 1959) il avait été signalé l'importance des teneurs en Radon des eaux naturelles et l'intérêt que l'on devait attacher à la "dose de tolérance". De toute façon, il semble bien que nous possédons maintenant un appareillage et une méthode permettant le contrôle de la teneur en radon (et en radium) des eaux naturelles (Roubault *et al.*, 1958).

Résumé

Exposé d'une méthode de terrain destinée à la détermination de la teneur en radon d'eaux naturelles. Les résultats obtenus au cours de deux campagnes dans diverses régions de France sont étudiés par les moyens de la statistique. Il apparaît alors que: (1) Les teneurs en radon se distribuent lognormalement dans une formation géologique donnée. (2) Le dosage du radon dans les eaux est susceptible de devenir une technique de prospection. (3) Les teneurs en radon des eaux sont très souvent supérieures à celles admises en biologie.

Des études systématiques sur la détermination du radon dans les eaux naturelles de diverses formation géologiques ont été entreprises depuis quelques années (1957–1959) au Centre de Recherches Radiogéologiques de l'Université de Nancy. Ces recherches ont essentiellement porté sur l'adaptation de méthodes aux conditions difficiles du terrain ainsi que leur application en des régions très diverses. Un certain nombre de résultats avaient permis de tirer quelques conclusions (Roubault *et al.*, 1959) ce travail leur fait suite en les complétant.

Nombreux sont les procédés employés pour doser le radon dans les eaux, l'atmosphère des roches et des sols. Mais ils sont, soit déjà anciens, lents—chambre d'ionisation (Delibrias, 1954) (couramment employés en U.R.S.S. dans l'émanométrie) soit exigeant un matériel fragile et délicat donc de déplacement sur le terrain difficilement réalisable—chambre d'ionisation à impulsion (Hudgens *et al.*, 1951).

Nous avons été amenés à utiliser, en nous inspirant des travaux de Damon et Hyde, (1952) et de Van Dilla (1955), le comptage par scintillation α en utilisant des

récipients dont la paroi interne est tapissée de sulfure de zinc. Ces récipients sont en verre et constituent la chambre de mesure couplée optiquement à un détecteur de scintillation de réalisation courante, une échelle démultiplicatrice complète l'ensemble.

Bibliographie

Arndt R. M. et Kuroda P. K. (1953) Radioactivity of rivers and lakes in parts of Garlands and Hotsprings counties, Arkansas. *Econ. Geol.* **48,** 551–567.

Bernard A., Jurain G. et de la Roche H. (1959) Rappel de notions fondamentales et généralités sur la prospection géochimique. *Colloque sur la Prospection Géochimique, Abbaye de Royaumont* 1959.

Budde E. (1956) Radon measurements as method in geophysics. *Comm. Eleventh European Association for Exploitation of Geophysics*, Milan.

Combrisson J. (1955) *Recueil de données numériques et de définitions. Protection. Dosimétrie.* Rapport CEA no. 455, CEN Saclay.

Coulomb R. (1955) Dispersion des radioéléments de la famille Uranium-Radium dans les eaux naturelles. *Bull. Soc. Fr. Minéral.* **78,** 89–96.

Damon P. E. et Hyde H. I. (1952) Scintillation tube for the measurement of radioactive gases. *Rev. Sci. Instrum.* **23,** No. 12, 766.

Delaby R., Charonnat G. et Janot M. (1931) La radioactivité des eaux de quelques sommets des Vosges. *C. R. Acad. Sci., Paris* **193,** 1434–1436.

Delaby R., Charonnat G. et Janot M. (1932) La radioactivité des eaux du Ballon d'Alsace. *C. R. Acad. Sci., Paris* **195,** 1294–1297.

Delaby R., Charonnat G. et Janot M. (1933) Nouvelles recherches sur la radioactivité des eaux du massif du Ballon d'Alsace. *C. R. Acad. Sci., Paris* **197,** 1294–1297.

Delibrias G. (1954) Dosage du radon dans l'air. *J. Phys. Radium* **15,** 784–80 A.

Dormois R., Poughon A. et Zegers J. (1959) Rapport technique inédit, Mission DREM, CEA en Pologne.

Grammakov A. C., Kvashnevskaya N. V., Nikonon A. I., Sokolov M. M., Sochevanon N. N., Suppe S. A. et Tafeyev G. P. (1958) Some theoretical and methodical problems of radiometric prospecting and survey. *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva* Vol. II, pp. 732–743. United Nations, New York.

Grimbert A. (1957) *Application des Techniques Géochimiques de Prospection à la Recherche et à l'Etude des Gîtes Uranifères en France Métropolitaine.* Note inédite, Commissariat à l'Energie Atomique No. 188 (par autorisation de M. le Directeur des Recherches et Exploitations minières, CEA).

Hilpert L. S. et Bunker C. M. (1957) Effects of radon in drill holes on gamma-ray logs. *Econ. Geol.* **52,** 438–455.

Hudgens J. E. R., Benzing R. O., Gali J. P., Meyer R. C. et Nelson L. C. (1951) Determination of radium or radon in gases, liquids or solids. *Nucleonics* **9,** No. 2, 14–21.

Jurain G. (1958) Signification géochimique des anomalies de teneur en Radon des eaux des massifs cristallins et cristallophylliens *C. R. Sommaire Société Géologique de France* No. 14 pp. 348–350.

Kirsch G. (1928) *Geologie und Radioaktivität* p. 214. J. Springer, Vienne.

Koechlin Y. (1955) Caractéristiques du montage optique d'un scintillateur. *J. Phys. Radium* **16,** 849–853.

Kuroda P. K., Damon P. E. et Hyde H. I. (1954) Radioactivity of the spring waters of hot springs National Park and vicinity in Arkansas. *Amer. J. Sci.* **252,** 76–86.

Leveau M. (1957) Détermination graphique des éléments intéressants d'une distribution lognormale lorsqu'on utilise l'ajustement de la droite de Henry. *Ann. Mines* **4,** 223–227.

Pradel J. (1956) *La Prospection de l'Uranium par le Radon.* Rapport CEA No. 588, CEN Saclay.

Roubault M., Coppens R. et Jurain G. (1959) Sur la teneur en radon des eaux froides de certaines régions de France. *C. R. Acad. Sci., Paris* **248,** 715–717.

Roubault M., Pascal J. et Coppens R. (1958) Sur une relation possible, directe ou indirecte entre le nombre de cas de leucémie et la radioactivité du sol. *C. R. Acad. Sci., Paris* **247,** 369–372.

Sanselme M. et Gerstner A. (1958) Les gisements d'uranium de La Chapelle Largeau et de la Commanderie (Deux-Sèvres). *Ann. Mines* **6,** 352–380.

Schepotjeva E. S. (1943) On the methods of radioactivity measurements. A vacuum method for measuring the content of radon in waters and gases. *Dokl. Akad. Nauk SSSR* **41,** No. 4, 169–171.

Stead F. W. (1955) Instruments et procédés de mesure de la radioactivité sur le terrain. *Proceedings of the First International Conference on the Peaceful Uses of Atomic Energy, Geneva* Vol. VI, pp. 820–828. United Nations, New York.

Stead F. W. (1958) Advances in radioactivity, radiochemical and isotopic methods of prospecting. *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva* Vol. II, pp. 32–34. United Nations, New York.

Tanner A. B. (1958) Increasing the efficiency of exploration drilling for uranium by measurement of radon in drill holes. *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva* Vol. III, pp. 42–45. United Nations, New York.

Geochimica et Cosmochimica Acta, 1960, Vol. 20, pp. 83 to 84. Pergamon Press Ltd. Printed in Northern Ireland

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